PB81-196792

Synoptic Survey of Chlorinated Hydrocarbon Inputs to the Southern California Bight Volume I: Summary Report

Southern California Coastal Water Research Project Authority, Long Beach

Prepared for

Corvallis Environmental Research Lab., OR

May 81

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PAGE NUMBER
EPA-287 (Cin.)
(4-76)

EPA 600/3-81-031a
May 1981

PB81-196792

SYNOPTIC SURVEY OF CHLORINATED HYDROCARBON INPUTS TO THE SOUTHERN CALIFORNIA BIGHT

VOLUME I SUMMARY REPORT

by

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Southern California Coastal Water
Research Project Authority
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Grant R803707

Submitted June 1976
Revised June 1980

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TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO.	2.	3. RECIPIENT'S ACCESSION NO.
EPA-600/3-81-031a	ORD Report	PB81 196792

4. TITLE AND SUBTITLE	5. REPORT DATE
Synoptic Survey of Chlorinated Hydrocarbon Inputs to the Southern California Bight, Volume I Summary Report	May 1981
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
David R. Young, Theadore C. Heesen, Deirdre J. McDermott	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Southern California Coastal Water Research Project 646 W. Pacific Coast Hwy. Long Beach, California 90806	11. CONTRACT/GRANT NO. R803707
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED final 10-72 to 5-76
Environmental Research Laboratory Office of Research and Development U.S. Environmental Protection Agency Corvallis, Oregon 97330	14. SPONSORING AGENCY CODE EPA/600/02

15. SUPPLEMENTARY NOTES

Minor revisions made June 1980

16. ABSTRACT

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17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Marine, Pollution, Chlorinated Hydrocarbons, DDTs, Dieldrin, PCBs, Chlorinated Benzenes, Municipal Wastewater, Industrial Wastewater, Surface Runoff, Aerial Fallout, Anti-fouling Paints, Harbors, Seawater, Sediments, Organisms.		

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
Release to Public	Unclassified	
	20. SECURITY CLASS *(This page)*	22. PRICE
	Unclassified	

EPA Form 2220-1 (9-73)

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ACKNOWLEDGEMENTS

Project consultants Dr. R. Risebrough and B. de Lappe (Bodega Marine Laboratory, Univ. of Calif. at Berkeley) have collaborated with us throughout the course of this investigation. The aerial fallout surveys were accomplished utilizing a collection technique developed by Dr. V. McClure (Natl. Marine Fish. Service, La Jolla, CA.). Intercalibrations were made with Dr. S. Pavlou (Univ. of Washington, Seattle), Dr. J. Blazevitch (EPA, Seattle), Dr. P. Taylor (Calif. Analytical Labs., Sacramento), and Dr. J. McGuire (EPA, Athens, GA.). Prof. J.D. Isaacs (Scripps Inst. of Oceanography, La Jolla, CA.) stimulated our investigations into discharges of para-dichlorobenzene.

We have been assisted by numerous chemists and oceanographers from the several sanitation districts involved in this study, including D. Hotchkiss, I. Haydock, R. Stewart, and D. Fisher (County Sanit. Dist. of Los Angeles Co.), J. Nagano (Hyperion Treatment Plant, City of Los Angeles), G. Pamson, F. Tanner, and R. Young (Orange Co. Sanit. Dist.), W. Conn (Pt. Loma Treatment Plant, City of San Diego) and Dr. G. Cianko (Oxnard Treatment Plant). In addition, we thank A. Leipzig (Sanit. Dept., City of Los Angeles), J. Mitchell (Los Angeles Co. Flood Control Dist.), Dr. L. Schinazi (Los Angeles Reg. Water Qual. Control Bd.), J. Barry (San Diego Reg. Water Qual. Control Bd.), and R. Williams and E. Amadon (U.S. Geol. Survey) for assistance in obtaining samples and discharge data.

The following individuals obtained aerial fallout samples from the islands off southern California: Dr. R. de Long (Nat. Marine Fish. Service, Seattle); L. Laughlin (Channel Is. Field Station, Univ. of Calif., Santa Barbara); W. Connally and M. Connally (Is. Packers Co., Ventura); Superintendent W. Ehorn (Nat. Park Service, Channel Is. Nat. Monument, Ventura); Chief R. Anderson (U.S. Navy, San Nicolas Is.); Dr. R. Given (Santa Catalina Marine Lab., Univ. of So. Calif., Los Angeles); and Lt. Comdr. W. Kay (U.S. Navy, San Clemente Is.). G.C. Barragan (Universidad Autonoma de Baja California, Ensenada) collected the Ensenada samples.

Project personnel contributing to this research include: W. Bascom, Director; C. Halgren; chemists R. Johnson, I. Szpila, E. Berkihiser E. Leong, J. Wright; data analyst P. Hershelman; biologists Dr. A. Mearns, M. Sherwood, J. Allen; engineers, J. Mardesich, H. Stubbs, Dr. T. Hendricks; field samplers M. Moore, H. Schafer, J. Johnson, M. Westbrook, P. Smokler, R. Voglin, R. Gammon.

This research was conducted under a grant from the U.S. Environmental Protection Agency; we thank our Project Officer Dr. D. Baumgartner (Chief, Marine and Freshwater Ecology Branch) for valuable suggestions made throughout the study.

Contribution No. 59 of the So. Calif. Coastal Water Res. Proj.

SECTION I

INTRODUCTION

The principle objective of this study was to determine the major input routes and rates of potentially-toxic chlorinated hydrocarbons to the marine ecosystem off southern California, known as the Southern California Bight. The coastal plain bounding this ecosystem is inhabited by approximately 12 million persons, or about 5 percent of the nation's population. The resulting high level of domestic, industrial, and agricultural activity in this region has led to significant contamination of the nearshore marine waters by a variety of potential pollutants (SCCWRP, 1973), including residues of the pesticide DDT and mixtures of the industrially important polychlorinated biphenyls (PCB). The input routes which we investigated were municipal wastewater, direct industrial discharge, vessel antifouling paints, harbor flushing, surface runoff, dry aerial fallout, and ocean current advection. Each of these routes is discussed individually in Sections V - XI of this report.

The second objective of this study was to gain a better understanding of the dispersion of chlorinated hydrocarbons following a major point source input to the coastal marine ecosystem. Because the Palos Verdes shelf off Los Angeles has received by far the largest such input yet reported in the United States, we concentrated our laboratory and field studies on samples from this region. The results are summarized in Section XII.

Finally, we have begun investigations on several other synthetic chlorinated compounds which are known to be: (1) Produced in relatively large quantities, (2) persistent in the environment, and (3) toxic. Results obtained to date in this area are presented in Section XIII.

Volume I of this report summarizes our findings, conclusions, and recommendations regarding the management of chlorinated hydrocarbons in coastal environments. Analytical procedures and supportive data and text are presented in Appendices A-J of Volume II.

SECTION II

SUMMARY

The results of our chlorinated hydrocarbon inputs studies conducted in southern California between 1971 and 1975 are summarized below:

		kg/yr			
Route	Year	Total DDT	Dieldrin	1242 PCB	1254 PCB
Muni. Wastewater	1972	6,540	100	≥19,200	≥260
Muni. Wastewater	1973	3,830	≤280	≥ 1,900	1,510
Muni. Wastewater	1974	1,580	95	4,270	1,120
Muni. Wastewater	1975	1,150	-	2,400	680
Industrial Disch.	1973-74	40	10	≤70	30
Antifouling Paint	1973	<1	-	<1	<1
Surface Runoff	1971-72	100	20	100-170	90-110
Surface Runoff	1972-73	320	65	0-550	250-280
Aerial Fallout	1973-74	1,800	-	-	1,800
Ocean Currents	1973	≤7,000	-	-	≤4,000

Of about a dozen of the most common pesticides sought, only DDT residues (total DDT) and Dieldrin were routinely identified in any significant quantities. The PCB's observed most closely resembled mixtures averaging 42 and 54 percent chlorination.

Coastal distributions of total DDT in intertidal mussels, sediments, crabs, and flatfish showed distinct gradients, with concentrations increasing sharply toward the JWPCP submarine outfalls off Palos Verdes Peninsula. This discharge, which carried about 22 m tons of total DDT during 1971, has contributed more than 99 percent of the DDT measured in municipal wastewater released to the Bight, and the input of this pesticide has been detected more than 100 km from the Peninsula. Approximately 200 m tons of total DDT are still contained in bottom sediments of the JWPCP monitoring zone (60 sq km), apparently the result of waste discharge to the sewer system from a large pesticide plant. Although this discharge was stopped in 1970, the gradual flushing of contaminated sewer sediments caused the JWPCP outfalls five years later to remain the dominant wastewater source of DDT to the Bight.

Since 1972 estimated DDT and PCB inputs from the Palos Verdes outfalls have decreased by factors of 6 and 12, respectively. However, both sediment and flatfish concentrations of both contaminants have decreased by only a factor of about 1.5 in the same period. Several species of bottom-feeding fishes in this region still exceed the 5 ppm limit for total DDT in seafood. Results of laboratory experiments are consistent with the observed persistence of chlorinated hydrocarbons in sediments.

Total PCB is a widespread contaminant of municipal wastewater; in recent years concentrations in most of the major systems have exceeded 5 ppb. To better detect and evaluate the presence of such synthetic organic contaminants in coastal marine ecosystems, we have successfully developed an offshore biomonitoring system using intertidal mussels. The vertical distribution of DDT and PCB residues in the water column around major submarine outfalls was found to be strongly dependent upon seasonal thermocline development and the type of wastewater discharged. In addition, harbor mussels still reflect past contaminations (often an order-of-magnitude above baseline), very possibly from past uses of PCB in antifouling paints and other vessel-related materials such as hydraulic fluids.

Dry aerial fallout of DDT and PCB residues was also found to be an important route of entry, with greatest inputs occurring off the highly populated Los Angeles - Orange County Basin. Fallout rates for total DDT were highest around a major manufacturing plant and one of its past landfill disposal sites. In contrast, the distribution of PCB fallout in the Basin did not reveal any dominant point sources. Aerial inputs of DDT since 1973 appear to be decreasing at an average rate of about 10 percent per year; PCB decreases have averaged only about 5 percent annually.

Finally, we have observed an additional class of toxic chlorinated hydrocarbon contaminants - the chlorobenzenes - in the major municipal wastewaters of the Bight. Concentrations of para- and ortho-dichlorobenzene each ranged from 2-12 ppb in the effluents, and similar levels of 1,2,4-trichlorobenzene have occurred in some effluent samples. Hexachlorobenzene concentrations generally were less than 0.4 ppb. Much lower levels of the chlorobenzenes were measured in urban runoff and aerial fallout.

SECTION III

CONCLUSIONS

1. In the past, submarine discharge of municipal wastewater has been the dominant source of chlorinated hydrocarbons such as DDT, Dieldrin, and PCB to the Southern California Bight. Dieldrin inputs have been of only secondary importance compared to those of DDT, and other chlorinated pesticide inputs have been insignificant. PCB contamination of these wastewaters is ubiquitous; in contrast, DDT inputs have been completely dominated by industrial wastes released by a single pesticide manufacture to the JWPCP sewer system.

2. Control of this input to JWPCP in 1970 has reduced the submarine injection of DDT contaminated particulates by more than 95 percent since 1971. PCB emissions (mostly 1242) via submarine outfalls have decreased by an order-of-magnitude since 1972, probably as a result of the 1971 restriction of PCB usage to closed systems.

3. Neither direct industrial discharges nor antifouling paints now appear to be significant sources of chlorinated hydrocarbons to the Bight. However, past use of PCB in such paints may have constituted a major input to the marine ecosystem, which the 1971 restriction has now controlled.

4. Surface runoff has made only secondary contributions of chlorinated hydrocarbons to the Bight, almost all from storm flow. The Los Angeles Basin has been the major source region, constituting approximately 85-95 percent of the individual inputs of total DDT, Dieldrin, and total PCB via this route.

5. Since 1974 dry aerial fallout has been the dominant route by which total DDT is transferred from southern California to the coastal ecosystem; for 1254 PCB this situation may have existed even earlier. However, 1242 PCB, a relatively volatile mixture, appears to have occurred at lower levels than 1254 PCB in recent aerial fallout and recent surface runoff. During 1975, greatest inputs of 1242 PCB still were being carried via municipal wastewater discharge.

6. The manufacture of DDT in Los Angeles County, and losses from past landfill deposits of resultant wastes, may be contributing significantly to coastal inputs of this contaminant via aerial fallout. In contrast, PCB inputs to the atmosphere appear to be much more diffuse. Fallout rates of both contaminants in this region are slowly decreasing.

7. Coastal inputs of chlorinated hydrocarbons in southern California have exceeded the amounts estimated to have been

transported from the north through the Bight via ocean currents.

8. DDT has been a serious pollutant of the waters off southern California, apparently affecting the reproduction of certain fish-eating birds and mammals, and contaminating seafoods caught near Los Angeles. Once the dominant input was identified and controlled, the main source of DDT became the sediments near the JWPCP outfalls. About 200 m tons were measured there in 1972. Levels are now slowly decreasing, possibly due to dispersion by storm waves. However, flatfish living in the discharge zone off Palos Verdes Peninsula in 1975 still averaged 10-15 ppm total DDT, 2-3 times the federal limit.

9. In contrast to the case for DDT, many sources release PCB to the southern California environment, making effective control a difficult task. The highest PCB levels in organisms (1-2 ppm) occur around major submarine outfalls and in harbors, despite significant reductions in PCB inputs to these regions. Contamination of the sediments again appears to be the main cause of this persistence.

10. Municipal wastewaters are also contaminated by another class of synthetic organics, the chlorinated benzenes. Levels of these hepatic and mitotic poisons usually exceed total PCB concentrations in such wastewaters. However, their specific toxicity is not well known or appreciated, and they are not yet included in chlorinated hydrocarbon monitoring programs.

11. Although several major coastal municipal wastewaters still exceed California's TICH standard for Total Identifiable Chlorinated Hydrocarbons (2 ppb, 50% occurrance; 4 ppb, 10% occurrance), our studies indicate that present DDT and PCB inputs to the Southern California Bight are not now causing muscle tissue concentrations in marine organisms to exceed the 5 ppm federal guideline for seafood. Thus, the TICH standard is adequate to meet the existing seafood limit, and probably is overly restrictive for certain effluents on that particular basis. However, ecologically meaningful guidelines are still lacking.

12. The TICH standard suffers from its lack of specificity and the fact that degree of compliance clearly depends on the sophistication of the wastewater analysis. Identification of previously unmeasured chlorinated compounds at relatively high concentrations, such as the chlorobenzene series reported here, puts the meaning of the TICH standard in doubt.

SECTION IV

RECOMMENDATIONS

1. Source control and use restrictions have greatly reduced marine inputs of DDT and PCB residues via wastewaters and vessel paints. Such efforts should be continued, with increased emphasis on limiting release to the atmosphere.

2. Uniform effluent standards should be replaced whenever possible by outfall-specific emission limitations which take into account dispersion characteristics of the outfall diffuser and discharge region.

3. Chlorinated hydrocarbons can persist in sediments and benthic organisms of discharge zones long after inputs have ceased; therefore the accumulation of particles containing these pollutants should be prevented.

4. Research on the effects of chlorinated hydrocarbons attached to particulates should be conducted to determine their toxicity.

5. Ecologically safe tissue concentrations of common chlorinated hydrocarbons in representative coastal organisms (such as intertidal mussels, benthic crustacea, bottom-feeding fishes) should be established to assist in evaluating discharge standards.

6. Biomonitoring systems utilizing filter-feeding animals caged at various depths in receiving waters should be evaluated for possible state-wide and national use.

7. Technical reviews of wastewater monitoring activities should be made periodically to increase the reliability of sampling and chemical determinations and provide periodic scans for new synthetic toxicants.

8. Research on ecological processes and effects of the major chlorinated benzenes in coastal waters should be initiated.

9. California's TICH standard is consistent with the Federal 5 ppm guideline for both DDT and PCB in seafood, but it should be reviewed in light of recent data on PCB toxicity. Corresponding guidelines are needed for the chlorobenzenes. As such information becomes available for specific chlorinated hydrocarbons, they should be removed from the TICH category and assigned an appropriate standard of their own.

SECTION V

MUNICIPAL WASTEWATERS

Every day, over 1 billion gallons (approximately 4×10^9 l) of municipal wastewaters are discharged from submarine outfalls to the Southern California Bight (SCCWRP, 1975). Almost 95 percent of these wastewaters are released by five major treatment plants, whose locations are shown on Figure 1. By sampling these five plants, we have been able to obtain a reasonably representative picture of chlorinated hydrocarbon inputs to the Bight via this route.

Generally twice a year since 1972, the Southern California Coastal Water Research Project (SCCWRP) has obtained one-week composites of effluent from each plant. Over each seven-day period, three to six grab samples of final effluent were collected daily in cleaned glass jars and refrigerated; at the end of the week, these samples were composited, extracted, and analyzed by electron capture gas chromatography, as described in Appendix A.

Intercalibration

Because of the significant analytical uncertainties associated with identification and quantification of chlorinated hydrocarbons in wastewaters, considerable effort has been devoted to intercalibration. In both 1971 and 1972, wastewater samples from the Joint Water Pollution Control Plant (JWPCP) of County Sanitation Districts of Los Angeles County (CSDLAC) were analyzed both at CSDLAC and at Bodega Marine Laboratory (BML) of the University of California at Berkeley. During 1973, replicate pairs of composited JWPCP wastewaters were analyzed at CSDLAC, BML, SCCWRP, and the University of Washington. The following year, one-week composite replicates from each of the five major treatment plants were analyzed at BML and SCCWRP; each effluent was also submitted to the laboratory of the plant from which it was taken. Later in 1974, and also twice during 1975, one-week composites again were collected and replicates analyzed at SCCWRP and at most of the plant laboratories. Detailed results of the various analyses are tabulated in Appendix B.

These studies indicated quite satisfactory agreement for the relatively low (ppb) concentrations of DDT and PCB compounds measured by the SCCWRP, BML, and University of Washington laboratories; the values reported typically agreed well within a factor of 2. CSDLAC monitoring data for the concentration of DDT and its residues (total DDT) in JWPCP wastewater since early 1971 also were confirmed. This is important, as these concentrations completely dominated those found in the other major effluents during our study. However, corresponding confidence in CSDLAC

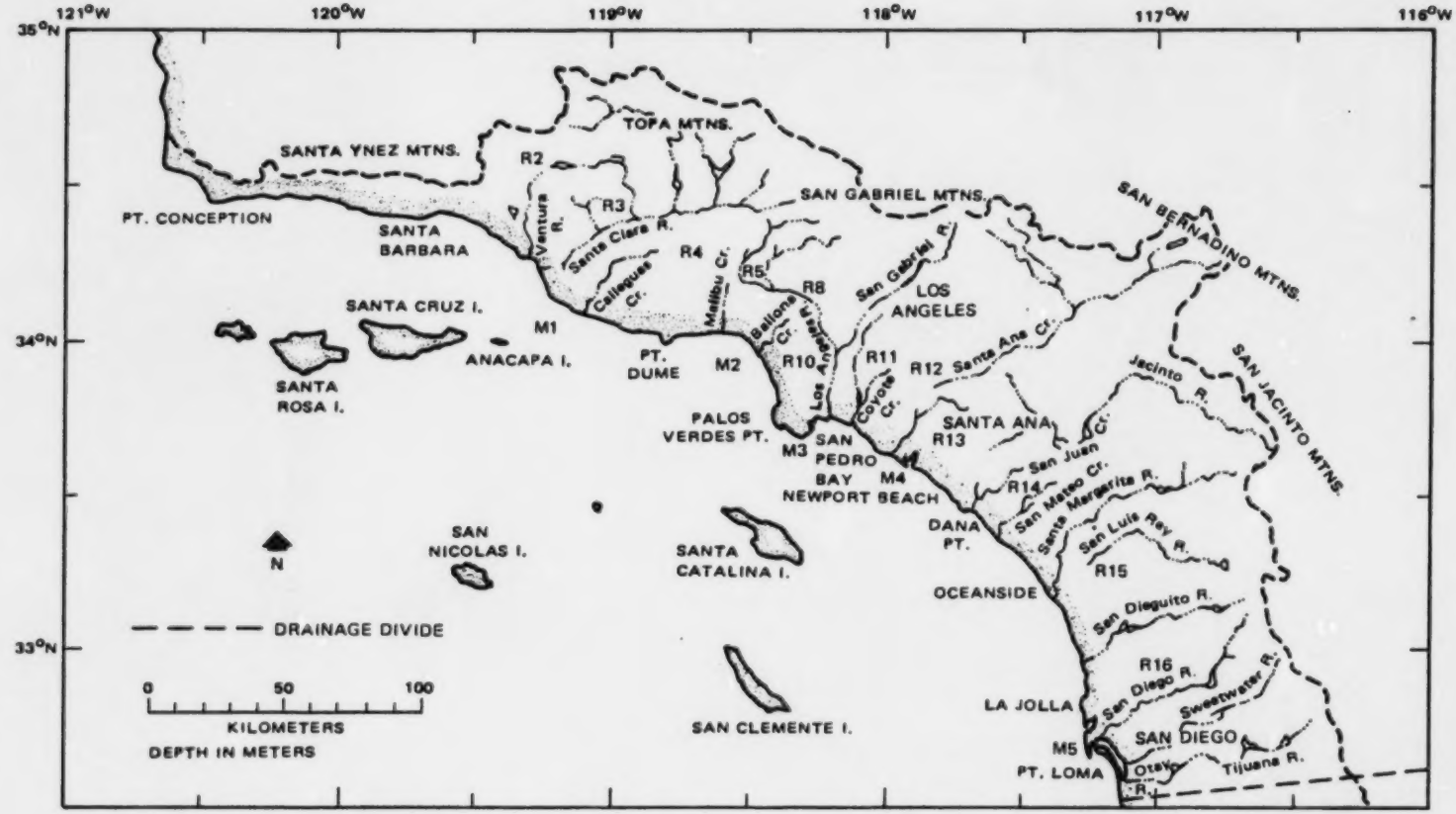

Figure 1. The Southern California Bight. Submarine outfalls of major municipal wastewater systems are: M1, Oxnard; M2, Hyperion; M3, JWPCP; M4, OCSD; M5, Pt. Loma. Major drainage basins (R2 - R16) are also shown.

monitoring data for total PCB in JWPCP effluent was not obtained until early 1975. Comparison of results from the laboratories which analyzed Orange County Sanitation District (OCSD) wastewater indicated that OCSD monitoring data for total PCB obtained at least since 1974 is reliable. However, significant discrepencies between results of the outside laboratories and monitoring data for effluent PCB concentrations from the Hyperion (City of Los Angeles), Point Loma (City of San Diego), and Oxnard City treatment plants through 1975 were observed (Young et al., 1975c).

Inputs

We have combined the results obtained by the SCCWRP, BML, and University of Washington laboratories as appropriate to obtain our best independent estimates of typical annual concentrations for total DDT, Dieldrin, 1242 PCB and 1254 PCB in final effluents from the major treatment plants. However, in view of the high and variable levels of DDT compounds in the JWPCP effluent, and our established confidence in CSDLAC data for this contaminant, we have used these monitoring data to obtain the JWPCP total DDT values for 1971-75. The resulting estimates, and also those for total suspended solids and discharge rate, are presented in Table 1. Corresponding estimates for annual mass emission rates (MER) via the five outfall systems are illustrated in Figure 2 and tabulated in Appendix B.

These results show that the JWPCP discharge off Palos Verdes Peninsula has dominated the other major municipal wastewater inputs of chlorinated hydrocarbons to the Bight. During 1971 almost 22 m tons of total DDT were carried via JWPCP final effluent to the shelf, and the 1972 JWPCP input (6.3 m tons) was two orders of magnitude above that of any other system. In 1972 the JWPCP outfalls also constituted the highest known municipal wastewater source of 1242 PCB to the coastal ecosystem; however, the OCSD and Hyperion outfalls also contributed significant quantities of this contaminant. Estimated inputs from the three systems were 11.6, 5.8, and 1.8 m tons, respectively.

As seen in Figure 2, the annual MER's of these two contaminants have decreased steadily since 1971-72. JWPCP inputs of 1254 PCB also appear to have decreased. The PCB reductions correlate with the reduced useage of polychlorinated biphenyls in "open" systems beginning in 1971 (EPA, 1976). However, the reduction in the DDT input from the JWPCP system apparently resulted almost entirely from the termination of a single industrial discharge to the CSDLAC sewer system in the spring of 1970.

Montrose Chemical

Although reliable monitoring of JWPCP effluent did not begin until January 1971, the evidence available indicates that prior to April 1970, Montrose Chemical Corporation was discharging on the

TABLE 1. CHLORINATED HYDROCARBONS (ug/l) IN MAJOR SOUTHERN CALIFORNIA MUNICIPAL WASTEWATERS

Discharger:	Year	Flow (mgd)[1]	Total Susp. Solids	Total DDT	Dieldrin*	1242 PCB	1254 PCB
JWPCP:	1971	372	320	42	-	-	-
	1972	351	290	13	0.14	24	ND**
	1973	359	260	7.5	0.35	3.9	1.6
	1974	346	280	3.0	0.04	1.9	0.76
	1975	341	280	2.3	-	0.97	0.41
Hyperion: (5-mile)	1972	330	88	0.21	0.03	ND	0.30
	1973	339	81	0.12	0.07	ND	0.38
	1974	341	83	0.12	0.03	0.11	0.24
	1975	345	85	0.07	-	0.16	0.18
Hyperion (7-mile)	1972	4.6	7,700	5.0	1.4	280	ND
	1973	4.8	7,500	1.4	4.8	ND	26
	1974	4.7	7,300	2.6	4.7	72	50
	1975	4.3	10,300	3.0	-	20	20
OCSD:	1972	150	150	0.36	0.03	28	ND
	1973	152	150	0.04	0.14	ND	1.4
	1974	171	110	0.23	0.25	8.0	0.89
	1975	176	140	0.04	-	6.5	0.81
Pt. Loma:	1972	95	140	0.26	0.02	ND	0.90+
	1973	100	160	0.18	0.09	ND	0.48
	1974	104	140	0.10	0.01	6.6	0.74
	1975	109	120	0.09	-	1.1	0.53
Oxnard:	1972	10	69	0.16	0.01	ND	0.20
	1973	12	130	0.48	0.01	ND	0.35
	1974	10	170	0.28	0.004	0.1	0.24
	1975	9.5	170	0.10	-	0.08	0.21

[1] Million gallons per day; 1 mgd = 1.38×10^9 l/yr

* 1973 Dieldrin values are upper limits due to incomplete separation from interferring compounds

** ND: Not detected

\+ Characterized as Aroclor 1260

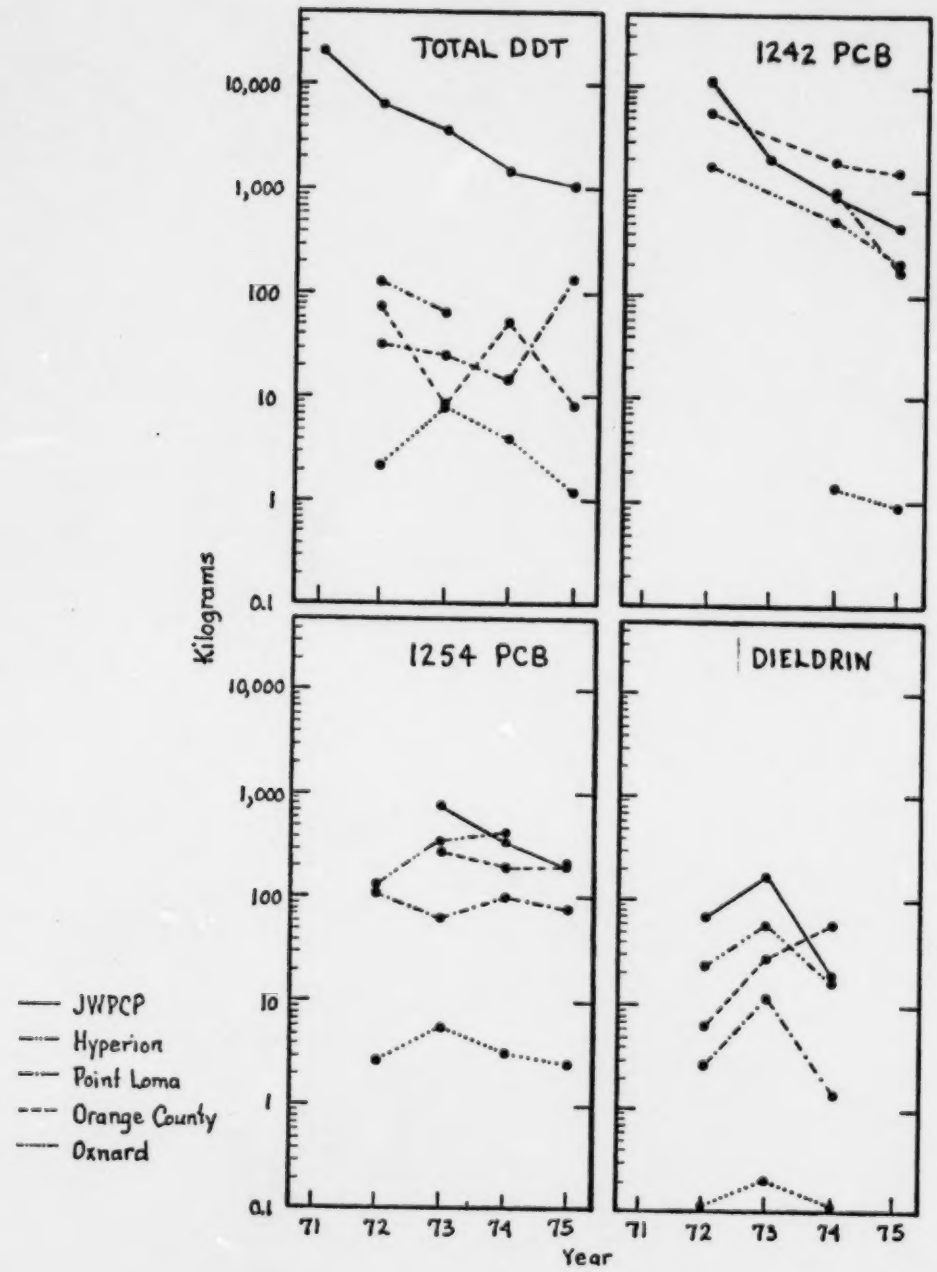

Figure 2. Estimated annual mass emission rates of chlorinated hydrocarbons in major municipal wastewaters discharged to the Southern California Bight, 1972-75.

order of 300 kg/day total DDT to the CSDLAC sewer system from its pesticide plant located in the City of Torrance. Twenty-four hour composite samples collected from the system above and below Montrose on March 30, 1970 indicated that at this time the plant was discharging approximately 290 kg/day of total DDT to the wastewater system. Although this was the only such sampling conducted before Montrose began hauling its caustic liquor wastes to a landfill disposal site in April 1970, analysis of a sample of this caustic liquor waste taken directly from the Montrose waste stream on August 4, 1970 indicated a total DDT concentration of 3,400 ppm (mg/l). This corresponds to a total DDT emission rate of about 270 kg/day for an average quantity of caustic liquor waste of 83,000 l/day, in good agreement with the earlier estimate (CSDLAC, Jan. 1973). The Montrose plant was built around 1950.

Unfortunately, records of previous Montrose discharges to the wastewater system are not available. However, sewer sediments collected at two stations downstream of Montrose on May 14, 1971 respectively contained 165,000 ppm (16.5 percent) and 130,000 ppm (13 percent) on a dry weight basis, compared to 300 ppm (0.03 percent) found just upstream of Montrose (CSDLAC, May 1971). A subsequent sampling of two stations downstream of Montrose on July 15-16, 1971 revealed sewer sediment total DDT concentrations of 32 percent and 39 percent, respectively, suggesting that almost 30 m tons of total DDT were contained in the sediments of the 200 m stretch of pipe between the two stations (CSDLAC, Dec. 1972).

Following the April 1970 initiation of landfill disposal of the Montrose caustic liquor waste, estimates of total DDT discharges by Montrose (based on upstream and downstream collections) decreased significantly, from 290 kg/day on March 30 to 20 kg/day on July 27 (CSDLAC, Dec. 1970). However, direct analysis of Montrose effluent indicated that the reduction in the DDT input rate to the sewer was actually much greater than indicated by the above data. A twenty-four hour composite collected on August 14, 1970 yielded a daily input value of 0.1 kg total DDT, and eight such composites collected between August and December 1970 indicated an average input of 0.2 kg/day (CSDLAC, Jan. 1973).

Despite this very large reduction in DDT discharges to the system, the contamination of sewer sediments downstream from the Montrose connection apparently resulted in a much slower reduction in the annual emission of total DDT via the JWPCP effluent. Five years after the termination of the Montrose input, the MER of total DDT to the Palos Verdes shelf (approx. 1 m ton/yr) was still more than 15 times that from the comparable discharge of Hyperion municipal wastewater into nearby Santa Monica Bay (approx. 0.06 m ton/yr).

SECTION VI

DIRECT INDUSTRIAL DISCHARGES

Most of the industrial wastewaters released directly to marine waters of southern California occur in San Pedro and San Diego Harbors (Figure 1). These harbors also receive a wide variety of industrial discharges. Thus, we were able to study a number of different types of industrial effluents under similar conditions by surveying the two harbors.

More than twenty discharges into the Los Angeles and Long Beach sectors of San Pedro Harbor, and approximately ten discharges into San Diego harbor, have been investigated. To ensure accurate sampling, we enlisted the assistance of the government agencies holding jurisdiction over the various discharge areas to be sampled. In October 1973, field personnel of the Los Angeles Bureau of Sanitation provided composites of four hourly collections of effluents at twelve discharge sites in the Los Angeles Harbor. Access to discharge sites on Dominguez Channel in Long Beach Harbor was provided by the Los Angeles County Flood Control District, and similar composites of ten additional industrial effluents were obtained there by Project personnel. During August 1974, the major industrial discharges into San Diego Harbor were also sampled in this manner, with the assistance of the San Diego Regional Water Quality Control Board.

The industrial effluents were extracted and analyzed for identifiable chlorinated hydrocarbons. Results for individual discharges into San Pedro and San Diego Harbors are presented in Appendix C. Estimates for overall industrial inputs to the two harbors were obtained by calculating corresponding flow-weighted concentrations in up to six types of effluents. The flow-weighted concentrations were then multiplied by the reported total flows of each of these classes of industrial wastewaters into San Pedro and San Diego Harbors to obtain estimates of annual mass emission rates. The values are presented in Table 2.

Clearly, there are uncertainties involved in extrapolating the results of analyses of industrial effluent composites collected in a short time period to unsampled discharges and to an entire year. Unfortunately, the kind of assistance provided by municipal wastewater treatment plant personnel in obtaining reliable week-long composites upon request is not yet available from industrial dischargers. Provision for unlimited access to such samples by qualified researchers as a requirement for discharge would greatly enhance independent quantification of pollutant inputs. Nevertheless, these data provide no indication of significant releases of chlorinated hydrocarbons from the industrial effluents studied.

TABLE 2. CHLORINATED HYDROCARBON CONCENTRATIONS (ug/l) AND MER'S (kg/yr) IN DIRECT INDUSTRIAL DISCHARGES

Location: Constituent	Type of Discharge: Chemical Plant	Fish Cannery	Oil Industry	Power Plant	Shipyard	Misc.	Total
San Pedro Harbor - 1973							
Total Flow (mgd)	3.3	16	230	1,020	0.59	21	1,290
DDT: Conc	0.003	0.34	0.071	0.002	0.064	0.12	
MER	0.014	7.5	23	2.8	0.052	3.5	37
Dieldrin: Conc	0.002	0.008-0.020	0.025	0.001	0.011	0.031	
MER	0.009	0.18 - 0.44	7.9	1.4	0.009	0.90	11
1242 PCB: Conc	≤0.010	-	≤ 0.044	≤0.017	≤3.8	≤0.11	
MER	≤0.046	-	≤14.0	≤24	≤3.1	≤3.2	≤44
1254 PCB: Conc	0.024	<0.09	0.030	≤0.006	0.59	0.12	
MER	0.11	<2.0	9.5	≤8.4	0.48	3.5	14-24
San Diego Harbor- 1974							
Total Flow (mgd)	0.31	2.8	-	750	-	7.7	
DDT: Conc	0.026	≤0.004	-	0.0004-0.005	-	≤ 0.004	
MER	0.011	0.015	-	0.41 - 5.2	-	≤0.043	0.44-5.3
1242 PCB: Conc	≤0.003	≤0.018	-	≤0.028	-	≤0.002	
MER	≤0.001	≤0.070	-	≤29	-	≤0.021	≤29
1254 PCB: Conc	0.054	0.012	-	0.006-0.010	-	0.008	
MER	0.023	0.046	-	6.2-10	-	0.085	6.4-10

SECTION VII

VESSEL ANTIFOULING PAINTS

In 1973, we surveyed most of the drydock or haulout facilities serving naval, commercial, or recreational vessels in San Pedro and San Diego Harbors, as well as those serving recreational vessels in Newport Harbor and Marina del Rey, the two largest small-craft anchorages in the Bight (Young et al., 1974). Our objective was to obtain a representative picture of antifouling paint usage in southern California. We obtained samples of the approximately forty brands of antifouling paint most commonly used at these facilities, as well as data on the number of craft in each harbor and the quantities of these paints applied annually.

The survey of antifouling paint application indicated that about 75 percent of the boats in the marinas investigated were painted once a year and that, on the average, approximately 4 liters of paint were used per boat. On the basis of this relationship and small craft inventories obtained from harbor masters, we estimated the use of antifouling paints in the twelve major marinas or harbors in the Bight; the results are presented in Table 3 (estimated quantities of antifouling paint applied annually to commercial and naval vessels in these anchorages are included in the estimates).

1242 PCB or 1254 PCB was detected in only seven of the twenty-eight wet paint samples analyzed (Appendix D). Levels were generally on the order of 1 mg/l or below; two samples had total PCB concentrations of approximately 40 mg/l. (Neglecting inequalities, median values for 1242 and 1254 PCB were 0.3 mg/l and 0.7 mg/l, respectively). When we combined these median values with the estimated quantities of antifouling paint applied annually to recreational, commercial, and naval vessels in marinas and harbors of the Bight, we obtained the estimated upper limits for PCB annual usage at each of the southern California anchorages (Table 3). Upper limit values for total DDT were an order-of-magnitude below those for total PCB.

Old Paints

Sixteen samples of antifouling paint scrapings collected from drydock facilities were also analyzed. Most of the PCB concentrations measured were less than 20 ppm. However, four samples yielded total PCB concentrations of 270, 3,300, 56,000, and 150,000 ppm, respectively. Furthermore, the two highest concentrations of 1254 PCB that we found in the dried samples (approximately 5 and 15 percent on a dry weight basis) correspond with an observation by Dr. V. McClure (National Marine Fisheries Service, La Jolla, CA., personal communication), who found that a paint chip collected in a zooplankton trawl in 1970 contained

TABLE 3. ANTIFOULING PAINT PCB APPLIED IN SOUTHERN CALIFORNIA HARBORS

Basin No.*	Harbor	Paint Applied** (l/yr)	PCB's Applied (g/yr) 1242	1254
R-1	Santa Barbara	2,300	0.7	1.6
R-2	Ventura	2,800	0.8	2.0
R-4	Oxnard	2,800	0.8	2.0
R-8	Marina del Rey	16,700	5.0	12
R-8	Redondo-King	4,200	1.3	3.0
R-10	San Pedro	141,000	42	98
R-11	Huntington	9,700	2.9	6.8
R-13	Newport	24,200	7.3	17
R-14	Dana Point	1,700	0.5	1.2
R-15	Oceanside	1,700	0.5	1.2
R-16	Mission Bay	4,500	1.4	3.2
R-16	San Diego	84,000	25	58
	Total	295,000	88	206

* Harbor located near this basin, which is shown on Figure 1.

** The values for San Pedro and San Diego Harbors include estimates for commercial and naval vessels (116,000 and 73,000 l/yr for the two harbors, respectively).

approximately 10 percent PCB. Polychlorinated biphenyls are reported to have been used extensively as a plasticizer in paints before such use was banned in this country in 1971.

The data in Table 3 indicate that approximately 300,000 liters of antifouling paints are applied to vessels annually throughout the Bight. Our survey revealed that, on the average, the density of antifouling paints used in southern California is about 1.5 dry kg/l. Therefore, if such paints did contain 10 percent PCB in the past, an application rate of 300,000 l/yr would correspond to a PCB usage of 45,000 kg/yr (Young et al., 1976b).

Antifouling paints are designed to slough off with time, and an estimated 5 to 10 percent of the old paint removed from vessel bottoms is believed to be carried back to the harbor waters (Barry, 1972). Thus, although the actual PCB concentrations in paints used in southern California before the ban are not known, and despite the fact that an uncertain fraction of such materials are actually released to the water, these observations point to the possible importance of antifouling paints in the past as a source of PCB to the coastal marine environment. As seen in Table 2, discharges from shipyards in San Pedro Harbor had the

highest 1254 PCB concentrations of the industrial effluents surveyed. Old paints and/or hydraulic fluids may well have been the source. We have observed that the highest levels of PCB found in harbor mussels occur in regions of greatest vessel activity. For example, the whole soft tissues of mussels collected near vessel bottom scraping and repainting yards in Newport Harbor (Figure 3) and San Diego Harbor contained up to 20 times as much PCB as did those from mussels taken at nearby coastal sites (Young and Heesen, 1974; McDermott et al., 1975).

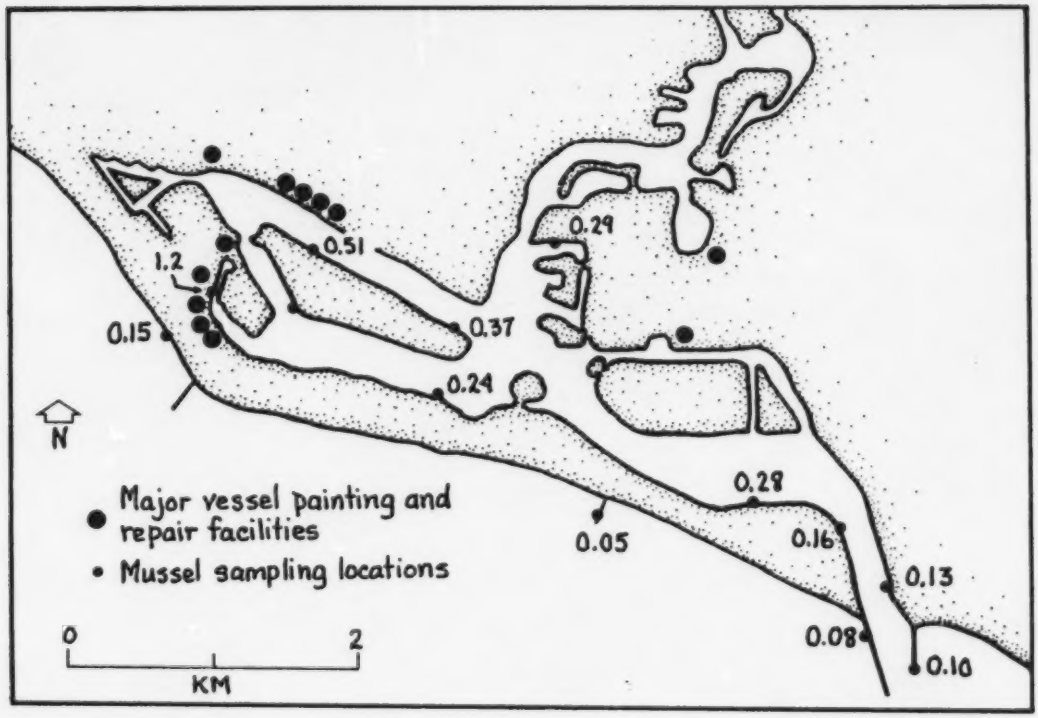

Figure 3. Total PCB concentrations (mg/wet kg) in soft tissues of M. edulis collected from Newport Harbor, January 1974.

SECTION VIII

HARBOR FLUSHING

In view of the relatively high levels of PCB contamination found in San Pedro, Newport, and San Diego Harbors, we attempted to determine if any significant levels of PCB could be detected in the waters moving from these harbors into the open ocean during periods of peak tidal flow. In the fall of 1974, we surveyed concentrations of these chlorinated hydrocarbons in surface seawater flowing through the mouths of the three harbors. The samples were collected in a cleaned stainless steel bucket from the bow of a small boat heading slowly into the current. Replicate 40-liter samples were collected over a semidiurnal period (five collections in approximately 12 hours) on the day when the greatest tidal difference of the month occurred. Current meter readings at mid-channel and mid-depth also were obtained over the collection period. These samples were concentrated on board the vessel by passing the seawater through polyurethane foam plugs in stainless steel columns at a rate of approximately 250 ml/min. The columns were then wrapped in aluminum foil, returned to our laboratory, and analyzed by the procedure described in Appendix A. This procedure was developed by B. de Lappe and Dr. R. Risebrough, BML, who have found it to be as efficient as batch extraction of chlorinated hydrocarbons from seawater (Appendix H).

Figure 4 illustrates the results obtained from the San Diego Harbor survey; net concentrations of 1254 PCB and total DDT for the replicate samples of each collection period are plotted against tidal flow (Young et al., 1975a). Although there is some evidence of increased PCB concentrations near the time of tidal reversal, when the greatest influence of "back harbor" water would occur near the harbor mouth, the measured concentrations were extremely low, at the part-per-trillion level (ng/l). Detailed results are presented in Appendix E.

We combined individual sample concentrations for each harbor with the corresponding volume of seawater that flowed during the three-hour period beginning one and one-half hours before each sampling to obtain amounts of total DDT and 1254 PCB that were transported. For each of these constituents, the sum of these individual mass transports was divided by the total flow, disregarding direction, for the entire twelve-hour period to obtain the flow-weighted mean concentrations for the three harbors. Resultant values for total DDT at San Pedro, Newport, and San Diego Harbors were 7.4, 8.3, and 0.5 ng/l, respectively. Corresponding values for 1254 PCB were 1.5, 19, and 1.8 ng/l. Freshwater runoff carrying large quantities of "terrestrial detritus" from a large storm which preceeded the Newport Harbor sampling may have caused abnormally high values there (McDermott and Heesen, 1975b).

By combining the measured concentrations with tidal flow values obtained from the current meter measurements and channel geometries, we obtained estimates for maximum net transport of total DDT and 1254 PCB from the harbors to the adjacent coastal ecosystem. Because of the extremely low concentrations observed, none of the values exceeded 25 kg/yr for total DDT or 50 kg/yr for 1254 PCB when extrapolated to an annual basis. Thus, these pilot seawater surveys have provided no indication that any of the three harbors is now a significant source of chlorinated hydrocarbons to the coastal marine ecosystem.

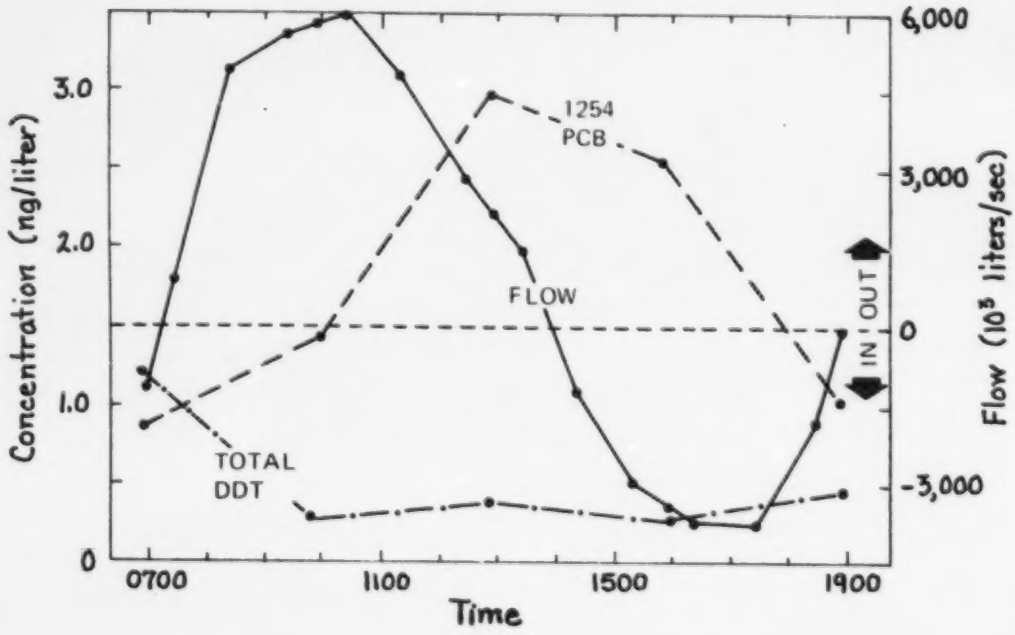

Figure 4. Chlorinated hydrocarbons in surface seawater collected from the mouth of San Diego Harbor over a semi-diurnal tidal cycle, November 12, 1974.

SECTION IX

SURFACE RUNOFF

In Water Year 1971-72, we conducted a detailed survey of chlorinated hydrocarbon inputs to the Southern California Bight via storm runoff. During the major storms of the year, time series of depth-integrated samples were collected in an all-metal sampler near the mouths of four major drainage channels--the Santa Clara River, Ballona Creek, the Los Angeles River, and the Santa Ana River (Figure 1). Analyses of the preserved samples were conducted by Dr. R. Risebrough and B. de Lappe at Bodega Marine Laboratory.

The following year, we resurveyed one of these channels on a limited basis. Los Angeles River runoff was sampled during four storms and analyzed in our laboratory. Subsequently, two seasonal collections of dry-weather flow were made from channels located throughout the Bight. Our analytical procedures are described in Appendix A.

Flow-Weighting

Final hydrographic data for both water years were obtained from local flood control districts and the U.S. Geological Survey. Figure 5 illustrates the pattern often observed--a correlation between concentrations of chlorinated hydrocarbons and suspended solids and rate of flow. In the case of the storm data, flow-weighted mean concentrations of the chlorinated hydrocarbons were calculated as the most representative characterization of the results, because the concentrations usually vary greatly during any given storm. For the dry-weather flow, values from the two seasonal collections were averaged for each channel or region.

Final flow-weighted mean concentrations of total DDT, Dieldrin, and total PCB in 1971-72 storm runoff are summarized in Appendix F. Table 4 lists flow-weighted mean concentrations for the four Los Angeles River storm flows sampled in 1972-73, and compares the yearly averages for this channel with those for 1971-72. Considering the variation in concentrations during any given storm, and the fact that two water years and two laboratories were involved, the agreement between the flow-weighted means is remarkably good. The 1972-73 means for each constituent in each storm flow agree within about a factor of 2, and the means for the successive years obtained from the BML and SCCWRP measurements generally are even closer.

In view of this agreement, we concluded that the results from the 1971-72 Bight-wide storm runoff survey could be safely extrapolated to the following year, on the basis of relative flow rates. The resulting 1972-73 mass emission rates are presented in Table 5.

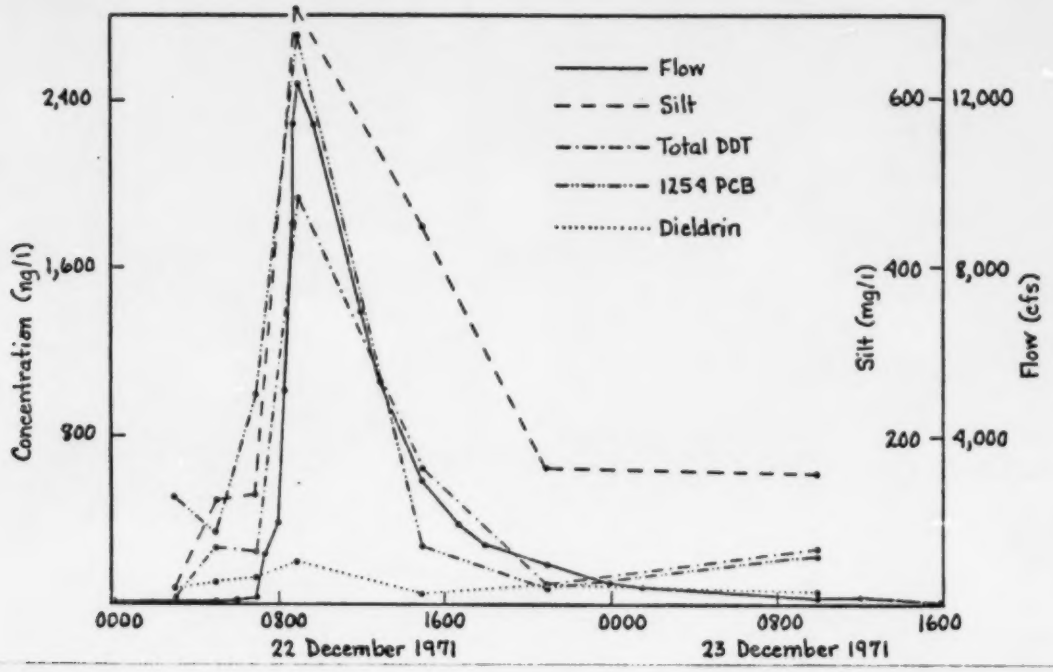

Figure 5. Chlorinated hydrocarbons, silt, and discharge rate measured in Los Angeles River storm runoff.

TABLE 4. FLOW-WEIGHTED MEAN CONCENTRATIONS (ug/l) OF CHLORINATED HYDROCARBONS IN LOS ANGELES RIVER STORM RUNOFF, 1971-73

Date	Total DDT	Dieldrin	1242 PCB	1254 PCB	Total PCB
4- 7 Dec '72	0.66	0.12	0-1.1	0.51	0.5-1.6
27 Feb to 1 Mar '73	1.5	0.16	0-3.2	1.0	1.0-4.2
6- 9 Mar '73	0.78	0.16	0-1.0	0.83	0.8-1.8
11-12 Mar '73	0.60	0.08	0-2.6	0.71	0.7-3.3
Average Blank	0.004	0.001	0.002	0.001	0.003
Averages					
1972-73	0.92	0.14	0-1.9	0.77	0.8-2.7
1971-72	0.93	0.16	1.2-1.9	0.9 - 1.1	2.1-3.0

TABLE 5. STORM RUNOFF MER'S OF CHLORINATED HYDROCARBONS BY CHANNEL, 1972-73

Basin No.	Channel	Volume (10^6cu m)	Total DDT Mean Conc. (µg/l)	Total DDT MER (kg/yr)	Dieldrin Mean Conc. (µg/l)	Dieldrin MER (kg/yr)	Total PCB Mean Conc. (µg/l)	Total PCB MER (kg/yr)
R-2	Ventura R.[b]	45.3		11.3-11.8		0.41		0-13.1
R-3	Santa Clara R.	93.4	0.25-0.26	23.4-24.3	0.009	0.84	0 - 0.29	0-27.1
R-4	Calleguas Ck.[b]	13.1		3.28-3.41		0.12		0-3.80
R-5	Malibu Ck.[b]	26.9		6.73-6.99		0.24		0-7.80
R-6	Topanga Ck.[b]	6.5		1.63-1.69		0.06		0-1.89
R-7	Sawtelle-Westwood Ch.[c]	11.6		4.41-4.64		2.32		5.45-10.6
R-8	Ballona Ck.	48.3	0.38-0.40	18.4 - 19.3	0.20	9.66	0.47-0.91	22.7 - 44.0
R-9	Dominguez Ch.[c]	15.7		5.97-6.28		3.14		7.38-14.3
R-10	Los Angeles R.	199	0.92	183	0.14	27.9	0.77-2.66	153 - 529
R-11	San Gabriel R.[d]	33.7		31.0		4.72		25.9 - 89.6
R-12	Coyote Ck.[c]	48.1		18.3 - 19.2		9.62		22.6 - 43.8
R-13	Santa Ana R.	16.7	0.16-0.18	2.67-3.01	0.077	1.29	0.11-0.23	1.84-3.84
R-14	San Juan Ck.[e]	6.0		0.96-1.08		0.46		0.66-1.38
R-15	San Luis Rey[e]	4.9		0.78-0.88		0.38		0.54-1.13
R-16	San Diego R.[e]	5.1		0.82-0.92		0.39		0.56-1.17
	ALL AREAS	574		313 - 318		61.6		241 -793[f]

a. 72-73 storm runoff concs. used for L.A. R., 71-72 concs. for other channels.
b. PCB conc. est. using data for Santa Clara R.
c. PCB conc. est. using data for Ballona Creek
d. PCB conc. est. using data for the L.A. R.
e. PCB conc. est. using data for the Santa Ana R.
f. Est. MER for 1254 PCB only: 241-274 kg/yr.

During spring and fall of 1973, dry-weather flow from twelve channels throughout the Bight was collected and analyzed. These data have been combined to yield average concentrations for dry-weather flow in those regions for which the 1972-73 volumes of nonstorm waters are known. From these data, we calculated the estimated mass emission rates of chlorinated hydrocarbons to the Bight via dry-weather flow in Water Year 1972-73; these results are summarized in Table 6.

The data in Table 5 show that during 1972-73 the Los Angeles River carried an order of magnitude more total DDT and total PCB via storm runoff than any other channel. Further, the estimated input of total DDT in storm runoff from the major channels in the Los Angeles Basin (Drainage Basins R-7 through R-12, Figure 1) was 260 kg, constituting 83 percent of the estimated total storm runoff input of this contaminant to the Bight. These channels also carried 81 percent of the dry-weather input of total DDT. For Dieldrin, the respective values were 93 percent and 96 percent; for total PCB, 92-98 percent and 75-84 percent, respectively. (Individual channel data are listed in Appendix F).

A comparison of mass emission rates for all areas via the dry-weather and storm runoff for Water Year 1972-73 is presented in Table 6. This summary illustrates that, although dry-weather flow constituted almost 20 percent of the total surface runoff volume during the year, it carried only about 2 percent of the total DDT, 7 percent of the Dieldrin, and 3 percent of the 1254 PCB. Thus, it appears that storm runoff is the dominant mode of surface runoff inputs of these synthetic organics to the Bight, and that the Los Angeles Basin is the principal source region.

TABLE 6. CHLORINATED HYDROCARBON MER'S (kg/yr) VIA STORM AND DRY-WEATHER RUNOFF, 1972-73

	Runoff			Dry Weather/ Total
	Storm	Dry Weather	Total	
Volume (10^6 cu m)	570	130	700	19 %
Total DDT	310-320	7	320-330	2 %
Dieldrin	62	5	67	7 %
1242 PCB	0-520	0-30	0-550	-
1254 PCB	240-270	7-8	250-280	3 %
Total PCB	240-790	7-38	250-830	1-15%

SECTION X

AERIAL FALLOUT

It is difficult to determine the amounts of contaminants deposited from the air directly into the ocean's mixed layer because of the problems in positioning samplers at an adequate number of stations throughout the study area. Fortunately, the Southern California Bight contains a number of islands which served this purpose. In this study, we used a collection technique developed by Dr. V. McClure (National Marine Fisheries Service, La Jolla, CA). The technique involves a clean glass plate, which is sprayed with a 5:1 mixture of hexane and mineral oil and exposed to dry fallout for a specified period. The mineral oil is then collected with a teflon scraper and analyzed according to the procedure described in Appendix A.

Replicate plates 0.1 sq m in area were exposed for about one week at an elevation of about 4 m on structures at thirteen coastal and five island stations between Point Conception and the U.S./ Mexico border. Two thirteen-week surveys were conducted in summer 1973 and spring 1974, and a three-week survey was conducted during fall 1974. In addition, limited surveys were conducted during and after a major southern California brush fire in November 1975, and a series of seven replicate samples was collected at one coastal station off the Los Angeles-Orange County Basin during spring 1976. To ensure high recovery of the exposed mineral oil sample, we sprayed and scraped each collection plate three times in succession; numerous repetitions of this process indicated that scraping recovery exceeded 97 percent. In addition, detailed tests (described in Appendix G) were conducted to determine the retention efficiency of this technique. The one-week retention efficiency for the DDT metabolites analyzed (p,p'+o,p'-DDT, p,p'-DDE and p,p'-DDD) was generally over 60 percent. Although fallout rates of 1242 PCB were not obtainable, principally due to serious chromatographic interferences, the retention efficiency for 1254 PCB over a one-week exposure was estimated at about 50 percent. In most cases, blanks were a negligible fraction of sample concentrations (Appendix G).

Deposition Rate

During the first two surveys, net flux values for total DDT generally ranged between 40 and 200 ng/sq m/day; for 1254 PCB, they generally ranged between 50 and 150 ng/sq m/day. Values at certain coastal stations at the edge of the Los Angeles Basin were higher. During the third survey, however, values were higher by a factor of three for total DDT and two for 1254 PCB, on the average. The fall and winter seasons in southern California are characterized by desert winds (Santa Ana condition) which occur periodically and transport the polluted air of the

Basin out over the Bight. Weekly station values obtained for each metabolite during each survey are also listed in Appendix G.

In an effort to estimate the annual aerial input of total DDT and 1254 PCB to the Bight, we have used the median net flux value measured at each sampling site during each of the three surveys to calculate input values under non-Santa Ana (spring and summer) and Santa Ana (fall) conditions for the sectors shown in Figure 6. These sectors comprise an inner and an outer coastal zone, each almost 400 km in length and 50 km in width. (There were few stations in the outer zone; thus the input estimates for this area are considerably less reliable than those for the inner zone). Table 7 presents monthly mass emission rates, by sector, for the periods actually sampled. These data were utilized to estimate the annual mass emission rates, by sector, based on different wind conditions (Table 8). Overall annual input rates of total DDT based on non-Santa Ana and Santa Ana conditions are estimated to be 1,200 and 3,800 kg/yr, respectively. The corresponding input rates for 1254 PCB are 1,500 and 2,500 kg/yr, respectively. In southern California, Santa Ana conditions generally occur about 3 months out of the year in late fall and early winter. Applying respective weighting factors of 0.25 and 0.75 to the Santa Ana and non-Santa Ana condition values resulted in estimated annual inputs of 1,800 kg/yr for both total DDT and 1254 PCB to the study area via dry aerial fallout. (Rainfall is so infrequent in this region that its overall effect is judged to be negligible).

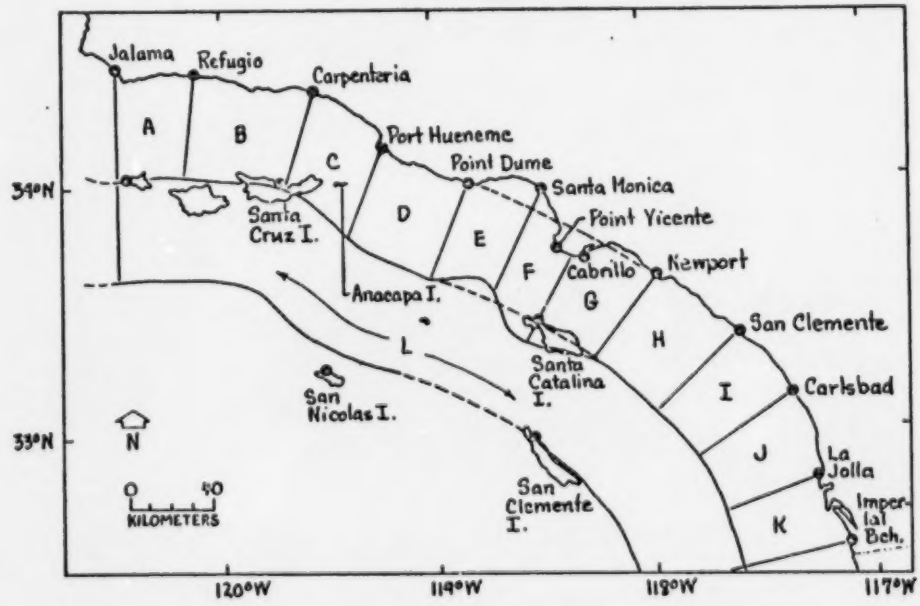

Figure 6. Collection stations and MER sectors used in aerial fallout surveys.

TABLE 7. CHLORINATED HYDROCARBON MER'S (kg/mo) VIA DRY AERIAL FALLOUT, 1973-74

Sector Code	Non-Santa Ana Conditions July-Sept '73 Total DDT	1254 PCB	Feb-Apr '74 Total DDT	1254 PCB	Santa Ana Cond. Oct-Nov '74 Total DDT	1254 PCB
A	3.1	4.8	3.2	3.7	8.1	6.0
B	4.7	6.5	6.2	5.7	13	12
C	5.3	7.6	9.2	6.1	25	15
D	7.1	9.2	11	7.2	29	17
E	9.2	7.0	8.3	11	17	13
F	7.0	5.2	6.4	8.3	17	12
G	10	6.8	15	9.2	52	26
H	7.6	8.2	6.4	6.2	34	16
I	5.3	7.0	4.8	4.5	22	12
J	3.7	6.0	5.3	5.7	8.3	9.2
K	2.3	4.3	3.4	4.7	11	9.2
Inner Total	65	73	79	72	240	150
L	18	52	22	53	83	60
Outer Total	18	52	22	53	83	60
Grand Total	83	125	100	125	320	210

TABLE 8. CHLORINATED HYDROCARBON FALLOUT MER'S (kg/yr) BY WIND CONDITION, 1973-74

Sector Code	Non-Santa Ana Conditions Total DDT	1254 PCB	Santa Ana Conditions Total DDT	1254 PCB	Estimated Annual MER Total DDT	1254 PCB
A	38	52	97	72	52	57
B	64	73	160	140	88	90
C	100	82	300	180	150	110
D	120	98	350	210	180	130
E	100	110	200	160	120	120
F	81	82	200	140	110	97
G	140	97	630	310	260	150
H	90	86	410	190	170	110
I	67	69	270	140	120	87
J	51	70	100	110	63	80
K	31	54	130	110	55	68
Inner Total	880	870	2,800	1,800	1,400	1,100
L	270	630	1,000	720	450	650
Outer Total	270	630	1,000	720	450	650
Grand Total	1,200	1,500	3,800	2,500	1,800	1,800

The estimated annual flux of total DDT at each of the sampling stations is shown in Figure 7. These data, and those of Table 8, show that the highest flux and input values for both chlorinated hydrocarbons generally occurred in the sectors off Los Angeles and Orange Counties and centered around the Palos Verdes Peninsula (sectors F and G). This portion of the coastal plain of southern California is most affected by air pollution. The 4,500 sq km area comprising the three sectors between Zuma Beach and Newport Beach, which accounts for only approximately 10 percent of the 40,000 sq km study area, received approximately 27 percent of the total DDT input and 20 percent of the measured PCB input. Thus, we find a pattern similar to that for surface runoff: The central basin appears to be the single most important source of DDT and 1254 PCB transported via the atmosphere to the waters of the Bight.

Interior Study

In view of the fact that PCB is an industrial chemical, it was understandable that the greatest aerial input should occur off the major population center. However, it was surprising that the same pattern should occur with DDT residues, which normally would be expected to peak off agricultural regions to the north and south. To investigate this matter further, we conducted a limited study within the Los Angeles Basin in the spring and fall of 1974 (Young et al., 1976c).

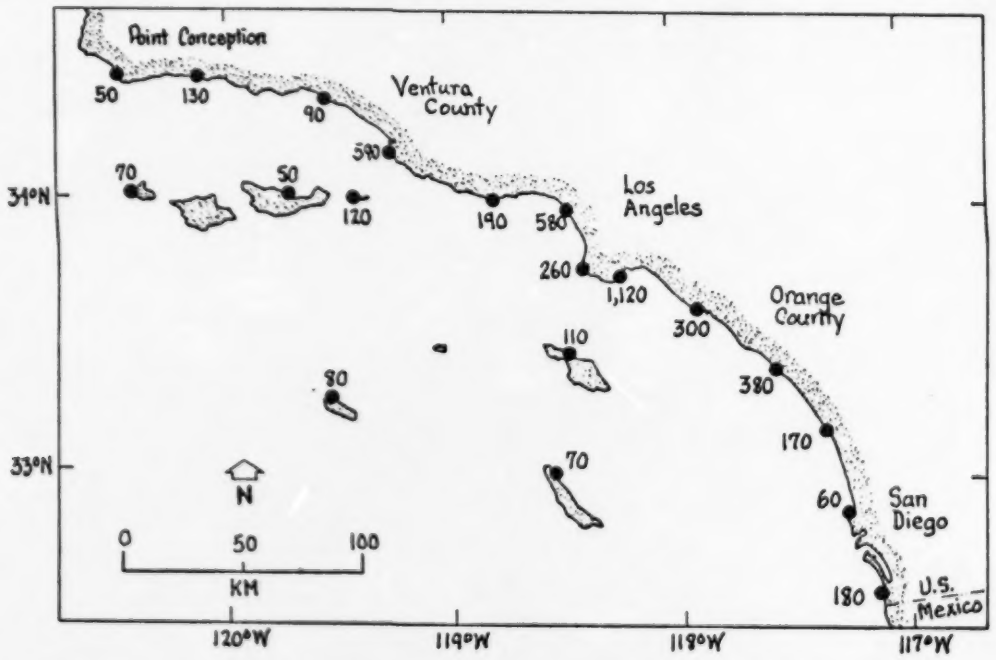

Figure 7. Estimated average annual flux of total DDT (ng/m^2-day) to the Bight via dry aerial fallout, 1973-74.

Between April 26 and May 24, we sampled twenty-four stations during four successive weeks. Because of the past history of dramatic DDT pollution of the Bight, apparently as a result of waste discharges from Montrose Chemical Corp., four stations were established within a few blocks of this industrial plant in the city of Torrance. Four sites also were established around the sanitary landfill in Rolling Hills Estates on the Palos Verdes Peninsula, operated by the County Sanitation Districts of Los Angeles County. This landfill received DDT wastes from the Montrose plant until the end of 1972. In addition, four sites were established around a private sanitary landfill owned by Ben K. Kazarian and located near the city of West Covina where the Montrose wastes have been taken since 1973.

In this survey, both the DDT constituents and 1254 PCB were clearly identified at levels at least on order of magnitude above those found in process blanks. The results showed two regions of relatively high DDT fallout, located in the vicinity of the Montrose plant and the Rolling Hills sanitary landfill. The highest of the values in each region generally occurred at the south or southeast stations. As the prevailing coastal winds are from the northwest, this suggests two separate sources.

In light of the large gradients in DDT fallout rates that were observed, and the implications regarding the sources, the survey was repeated during two weeks in September 1974; two additional stations were included in the pattern around the Montrose plant. The September DDT data were similar to those of the previous spring and indicate little seasonal effect.

Medians of the six weekly flux values for total DDT measured at each station are illustrated in Figure 8. These data clearly indicate an apparent relationship between the DDT fallout distribution and the location of a major manufacturing facility and one of its past waste disposal sites. However, the level of DDT in the dry aerial fallout around the present disposal site (the Kazarian landfill) was not any higher than levels at other Basin stations. As the two principal constituents of the pesticide itself are p,p'-DDT and o,p'-DDT, we examined these two products of the manufacturing process in greater detail. We found a considerably larger value for the ratio of p,p'-DDT to o,p'-DDT around the two regions of highest fallout (10 sites) than in the rest of the Basin (15 sites); median values for the two groups were 5.0 and 3.2, respectively. This ratio may be an indication of the relative "freshness" of the DDT constituents collected on our fallout plates. Similarly, the para and ortho isomers together constitute the largest percentage of total measurable DDT at these 10 sites; median percentages for the two groups were 85 percent and 63 percent. This too may be related to effects of "weathering". Finally, to determine if the relatively high DDT fallout values around the manufacturing plant and its past waste depository could be due merely to higher deposition

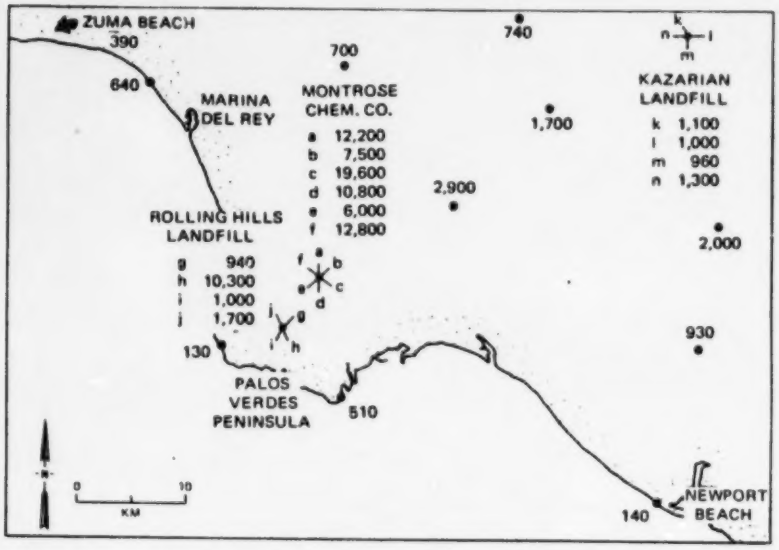

Figure 8. Median flux of total DDT (ng/m^2-day) via dry aerial fallout to the Los Angeles Basin during six weeks of 1974.

of particulates, we have normalized the values against 1254 PCB, which is not manufactured by Montrose. Distinctively higher values for this ratio were observed around the plant and the Rolling Hills landfill (median: 6.0) than in the rest of the basin (median: 1.2). Thus, it appears that the gradients in DDT fallout values we have observed do indicate two regions that are potentially important sources of DDT compounds to the Los Angeles Basin and the adjacent Southern California Bight. This is consistent with recent findings of a limited storm runoff study conducted in the Basin. Grab samples were collected on December 12, 1975, from a drain adjacent to Montrose and from four other drains located 1-2 miles from the pesticide plant. The latter samples yielded total DDT concentrations of 15, 28, 60, and 96 ppb, approximately 200 times lower than the 10,900 ppb measured in the Montrose sample. However, all four values were much higher than those obtained for Los Angeles River (<1 ppb).

Two methods were used to calculate the amount of total DDT falling onto the basin annually. The first involved a strict linear interpolation between data points. For those stations where there were two or more sampling sites, the median flux was used to represent the station. It should be noted that in the case of the Rolling Hills landfill, one site had a significantly higher flux than the other three sites. As this value is the median of six weekly values, and this site had the highest weekly flux

reported for the entire Basin study, it appears that the site represents a secondary source of DDT. However, the median flux of 1,400 ng/sq m/day is a more representative value for that station. Because the location of sampling sites and the high values at Montrose bias the fallout estimate of 2.2 metric tons/yr derived from contours, we consider this to be an upper limit. The median flux for the entire Basin, 930 ng/sq m/day, was used to estimate a lower limit. The fallout estimate calculated using this value is 0.5 metric tons/yr, resulting in an estimated range of 0.5 to 2.2 metric tons/yr (Young and McDermott, 1975).

One of the most important aspects of these findings is that there still may be a significant release of DDT wastes to the southern California environment from the manufacture of this pesticide in Los Angeles County, even though the discharge of liquid wastes to the County sewer system has been stopped. During 1974, the average level of total DDT in JWPCP final effluent was 3.0 ug/l, which alone exceeded California's standard of 2 ug/l (on a 50 percent occurrence basis) for total identifiable chlorinated hydrocarbons, TICH, in such wastewaters (California State Water Resources Control Board, 1972). The corresponding mass emission rate for total DDT was 1,400 kg/yr. We have estimated that a similar quantity (1,800 kg) of DDT compounds fell onto the coastal waters annually during 1973-74. A significant fraction of this material may have emanated from DDT wastes produced during manufacture of the pesticide in Los Angeles County, either directly from the plant or from its original land waste disposal site. Thus, a unified control plan to reduce marine inputs of this pollutant would require that attention also be paid to these potential sources of DDT to the atmosphere in Los Angeles Basin.

Fire Inputs

During November 1975, two of the largest southern California fires of the decade occurred in Angeles National Forest, burning 65,000 acres and depositing a distinct layer of ash throughout the Los Angeles Basin. To determine whether this kind of major aperiodic event could remobilize significant quantities of chlorinated hydrocarbons that previously had been deposited, a special fire sampling program was rapidly initiated to take advantage of this special situation. Sampling with our standard oiled plate collectors was begun on the same day (Nov. 24) as heavy deposition of ash began, and was terminated two days later when this visible deposition ceased. The sampling was then continued for another week for comparison. Santa Ana condition winds occurred throughout the period. Eight of our standard collection sites were occupied between Carpinteria and Carlsbad ; Santa Catalina Island was also successfully sampled (Figure 6). Detailed results are listed in Appendix G.

In general, it did not appear that there were any important changes in aerial transport of these contaminants as a result of

this major fire. When the fallout rates measured at the eight stations during the period of heavy ash deposition were compared to those observed at the same stations the previous fall, using the Wilcoxin signed-rank test, no significant differences were demonstrated. In contrast, during the same period fallout of seven trace metals all peaked sharply along the Los Angeles Basin coastline beneath the smoke plume, gradually approaching the constant non-fire baseline at the edges of the sampling region.

Recent Changes

In order to estimate whether or not there have been any important changes in the aerial input rates of total DDT or 1254 PCB to the Bight over the last three years, during spring 1976 we conducted a detailed resampling of the Newport Beach site. This station was selected because of the relatively low variability of its summer 1973 and spring 1974 values, and the fact that Newport Beach is situated at the southern edge of the Los Angeles - Orange County Basin, just downwind of the major population center found to be the dominant coastal source of chlorinated hydrocarbons to the atmosphere. Seven pairs of replicate samples were collected, yielding the following comparison with corresponding 1973-74 data:

Median Fallout Rate
Newport Beach (ng/m^2-day)

	Summer 1973	Spring 1974	Spring 1976	1976/1973	
Total DDT	214	219	158	0.74	$p < 0.05$
1254 PCB	111	114	97	0.89	$p > 0.20$

These results imply that since 1973-74 there has been a statistically significant decrease in the input of DDT residues to the coastal waters via dry aerial fallout; however, the rate of decrease at Newport Beach has been relatively low, averaging about 10 percent per year. An even lower annual decrease rate of about 5 percent was measured for 1254 PCB, and this decrease was not significant.

Comparison of Collectors

During October and November 1975, we conducted a series of six experiments to determine if fallout data obtained with the oiled glass plate collectors suffered from significant biases due to the relatively high temperatures which the exposed plates reached, or to the presence of mineral oil in the system. Therefore, we developed a new collector composed of an unoiled shallow aluminum pan which was constrained by a spring to rest continuously upon a

block of dry ice. The other surfaces of this block were sufficiently insulated so that the dry ice would last at least three days under normal conditions.

The three-day tests were conducted by exposing both this system and the regular oiled plate collector on the Project laboratory roof in El Segundo. Rate of deposition values for total DDT and 1254 PCB obtained from the glass plate system were corrected as usual by the appropriate time-dependent retention efficiency factors (in this case, 82 percent and 80 percent, respectively). Ratios of net flux values obtained from the cooled and uncooled samplers were calculated in each case. The average ratio (and its standard error) found for total DDT was 0.94 ± 0.10; for 1254 PCB, 0.84 ± 0.20.

These results show quite satisfactory agreement between the two very different systems for collecting DDT residues and 1254 PCB via dry aerial fallout. This agreement indicates that, relative to the unoiled, cooled collectors, the initial collection efficiency of the oiled glass system is neither significantly lowered by its considerably higher average temperature, nor significantly raised by the mineral oil coating which might absorb vapors of these chlorinated hydrocarbons directly from the overflowing air mass.

However, 1242 PCB has not been satisfactorily sampled by the oiled glass system in our region. We have very seldom obtained recognizable gas chromatographic profiles of this mixture in our collections, apparently due to interferences. Dehydrohalogination of the samples with alcoholic KOH typically caused reductions by almost a factor of 4 in the peak used to quantify 1242 PCB when a definite profile is obtained. In addition, data from the high volume air samples discussed in Section XIII showed that a much larger percentage of this interfering compound was in the vapor state than in the particulate (filterable) state, compared to corresponding percentages for total DDT and 1254 PCB. Thus, the unoiled, iced collector would appear to yield more representative estimates of the fallout rate of 1242 PCB (or its upper limit) than the oiled glass collector.

The results of the six tests described above for the unoiled, iced system showed that the median deposition rate for 1254 PCB at El Segundo during October and November 1975 exceeded that for 1242 PCB by at least a factor of 3.3; the corresponding factor obtained at Catalina Island in April 1976 also exceeded 3.3. In comparison, the storm runoff sampled from Los Angeles River during February 1976 carried at least 2.6 times as much 1254 PCB as 1242 PCB. These findings indicate that the majority of measurable PCB now being deposited via aerial fallout onto the southern California coastal plain and the adjacent marine waters is 1254 PCB.

SECTION XI

OCEAN CURRENT ADVECTION

As a part of this study, we attempted to estimate the quantities of measurable chlorinated hydrocarbons in surface seawater annually flowing through the Southern California Bight. In October 1973, we sampled surface seawater at seven stations along a north/south transect at the northwestern edge of the Bight. The transect began off Point Conception and ended approximately 300 km west of Oceanside. Circulation patterns (Jones 1971) indicated that the transect chosen should have intersected California Current water flowing into the Bight. However, during the first part of the cruise strong desert winds occurred which presumably increased the fallout rate of chlorinated hydrocarbons onto the sea surface.

Replicate 40-liter samples were collected in a stainless steel bucket, which was lowered from the bow of a research vessel that was slowly underway. Immediately upon collection, the replicate samples were passed through polyurethane foam columns in the manner described in Appendix A; they were subsequently taken to Bodega Marine Laboratory for analysis. The results, listed in Appendix H, indicate average concentrations for total DDT and 1254 PCB of 0.7 and 0.4 ng/l, respectively. However, the degree to which these values represent very recent aerial inputs from adjacent land areas in the Bight due to the desert winds cannot be determined.

These data may be used to obtain rough estimates of the quantity of these synthetic organics carried into the Bight via ocean current advection. Taking the length of the Bight as 500 km and the width influenced by the coast as 100 km, the effective study area is 5×10^4 sq km. Assuming the mixed surface layer to be 50 m, the volume of the mixed layer is 2.5×10^{12} cu m. It has been shown that the mean residence time of water in this mixed layer is on the order of 3 months (Jones 1971). Thus, the estimated advective flow rate of California Current Water through the Southern California Bight is 10^{13} cu m/yr, equal to 10^{16} l/yr. Corresponding estimates for advective flux rates of measurable DDT and 1254 PCB compounds are on the order of 7,000 and 4,000 kg/yr, respectively. In view of the fact that the seawater samples were collected from the upper meter during a Santa Ana (desert wind) condition, these values are probably upper-level estimates.

SECTION XII

DISPERSION

Extent

The data presented above indicate the degree to which the JWPCP outfall discharge has dominated inputs of total DDT to the coastal marine ecosystem off southern California. During the last five years we have studied the effects of this point source input on distributions of DDT residues throughout the Bight (SCCWRP, 1973; McDermott et al., 1974; Young et al., 1975b; Young et al., 1976d). Results for ocean bottom sediments, intertidal mussels, benthic crabs, and flatfish are illustrated in Figures 9 to 12.

These data clearly show the impact the JWPCP input has had on the distribution of DDT residues in this ecosystem. Typical levels in the intertidal and benthic animals were two orders-of-magnitude higher off Palos Verdes Peninsula than they were in control regions, and the median concentration of total DDT in the surface layer of bottom sediments in the JWPCP monitoring zone (26 ppm) was more than 3,000 times that measured in the Point Loma monitoring zone (0.008 ppm), approximately 150 km to the south. Comparison of the input and distribution data suggests that this contaminant of the JWPCP effluent was detectable more than 100 km from the discharge site. This is consistent with the relatively slow settling rates of chlorinated hydrocarbons, and the wastewater particulates with which they are associated, which we have measured in JWPCP and other effluents (Appendix I).

Benthic Contamination

The majority of the total DDT in both the organisms and the sediments was p,p'-DDE (Young et al., 1975b). A detailed survey off Palos Verdes Peninsula in summer 1972 indicated that approximately 200 m tons of total DDT were contained in the upper 30 cm of the bottom sediments in a 60 sq km region (McDermott et al., 1974). Dry-weight concentrations exceeded 200 ppm northwest (downcurrent) of the outfall diffusers, as seen in Figure 13. Corresponding values for 1254 PCB were approximately 10 ppm (Figure 14; Young et al., 1976a).

A resurvey of seventeen of the benthic grid stations in summer 1975 indicated that the typical (median) level in the surface layer had decreased by only a factor of 1.5 (Appendix I); in comparison, the average concentration of total DDT in the JWPCP effluent over a six-month period prior to each sediment survey (the "effective" input) decreased by a factor of 5.8. Further, the median concentration of total DDT in muscle tissue of Dover sole trawled from a corresponding region of the JWPCP discharge zone also decreased by a factor of 1.5 between May 1972 and

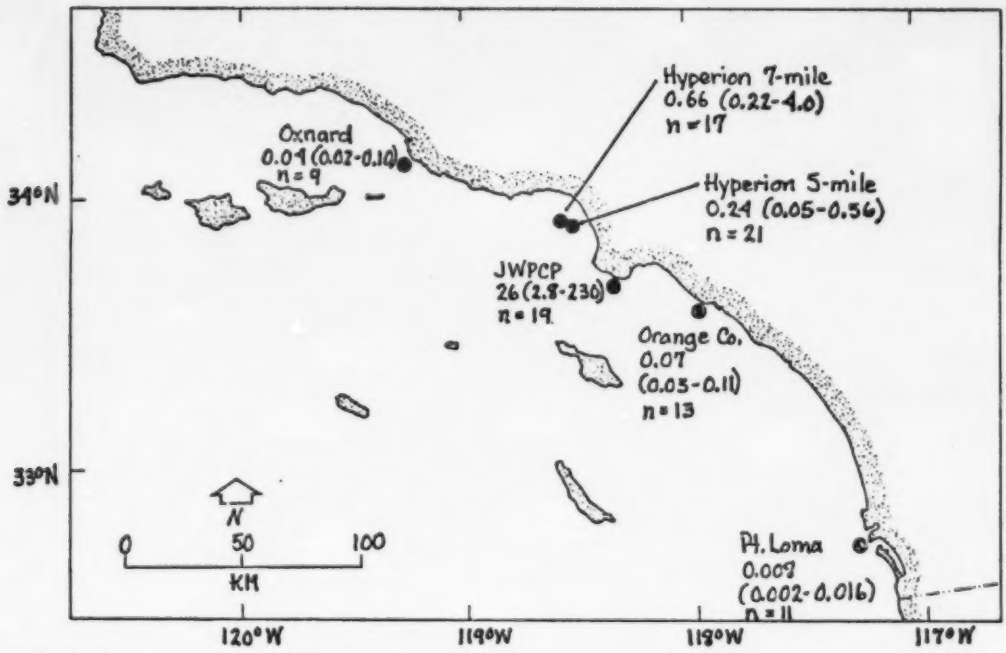

Figure 9. Median total DDT concentrations (mg/dry kg) in the surface layer (0-2 cm) of bottom sediments collected around major southern California outfalls, 1971-72. Ranges and number of samples (n) are also shown.

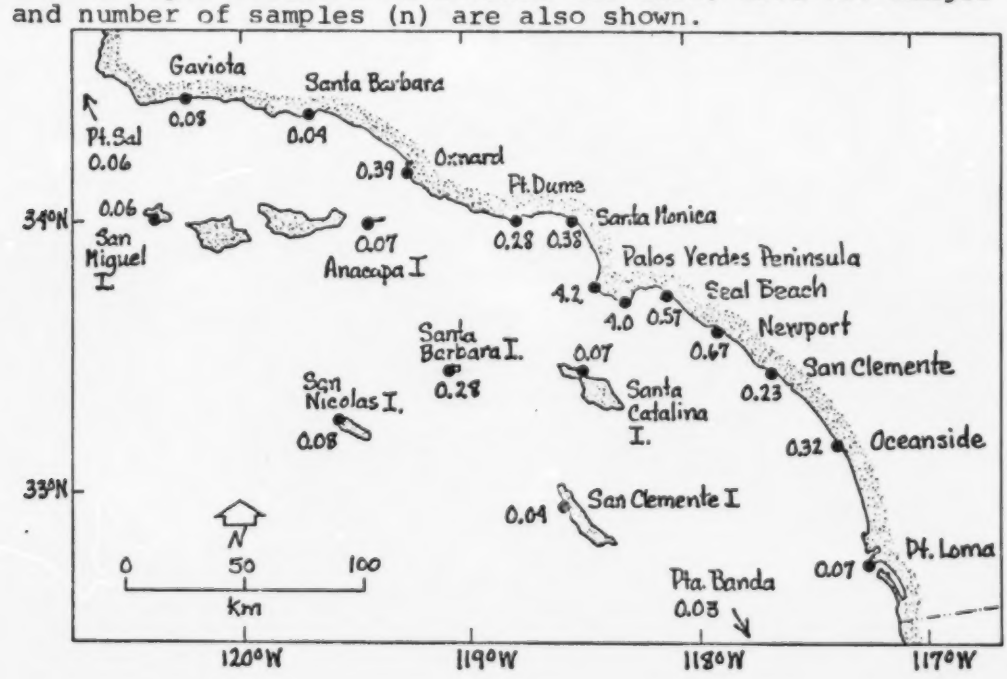

Figure 10. Total DDT concentrations (mg/wet kg) in soft tissues of the intertidal mussel M. californianus collected from the Bight, 1971.

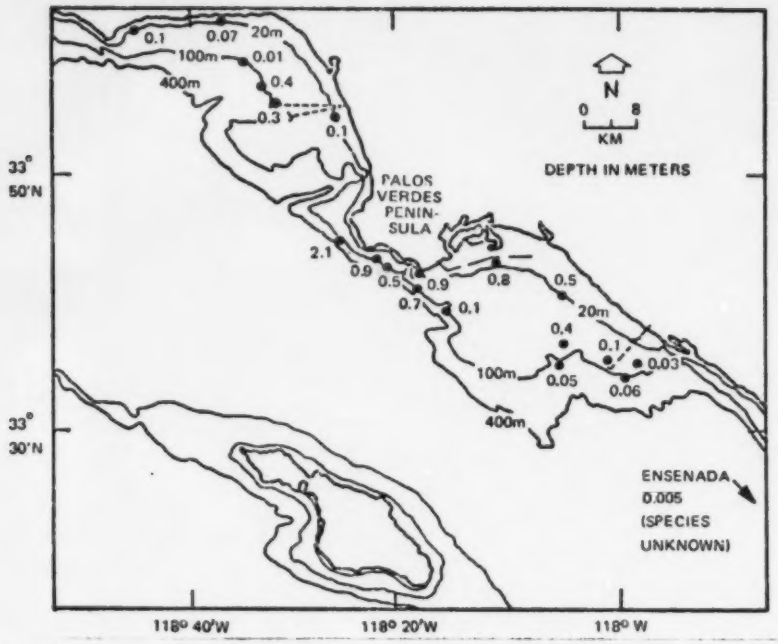

Figure 11. Total DDT concentrations (mg/wet kg) in muscle tissue of the benthic crab Cancer anthonyi collected off Los Angeles-Orange County Basin, 1971-72.

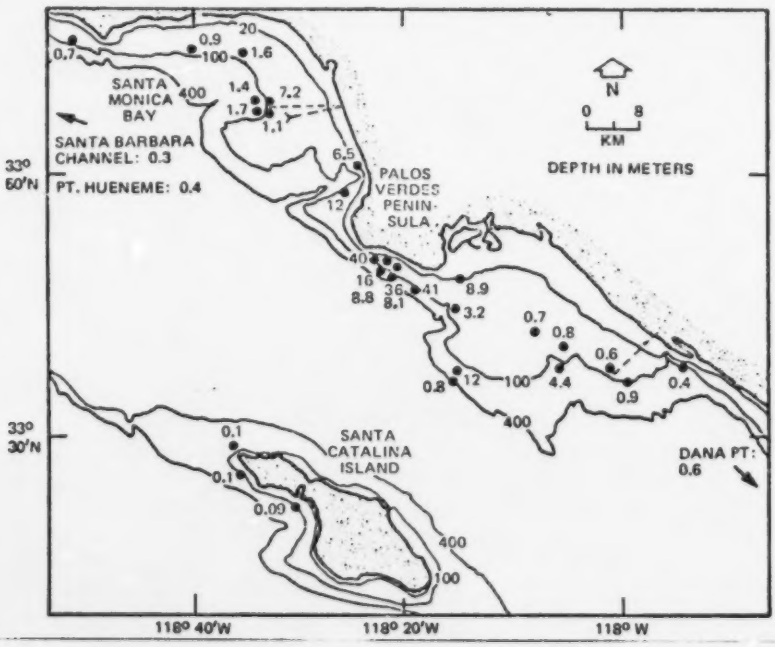

Figure 12. Total DDT concentrations (mg/wet kg) in muscle tissues of the Dover sole (Microstomus pacificus) collected off Southern California, 1971-72.

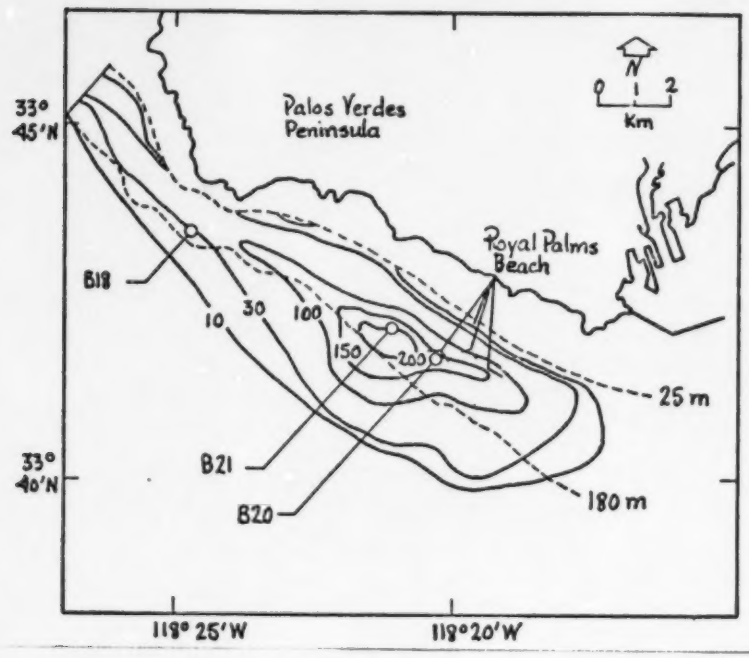

Figure 13. Total DDT concentrations (mg/dry kg) in surface sediments (0-2 cm) around the JWPCP submarine outfalls, 1972.

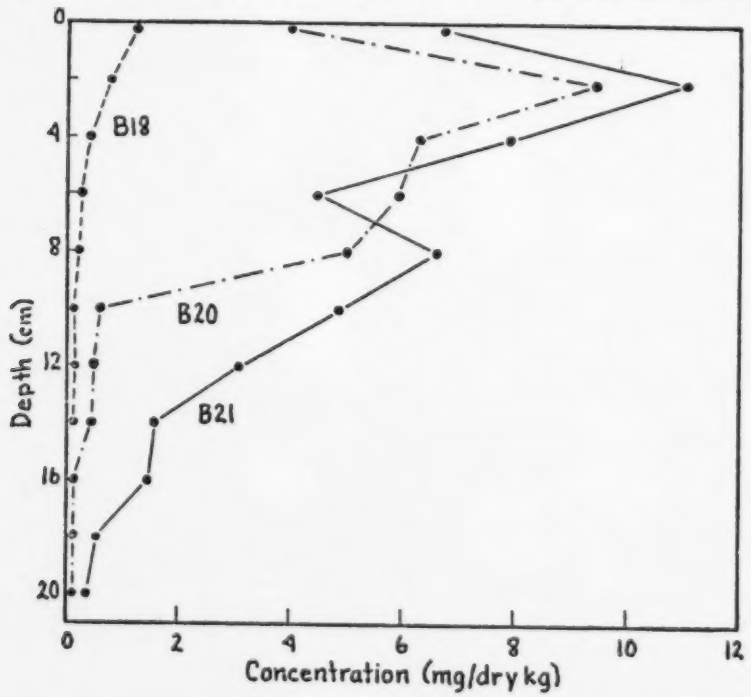

Figure 14. Vertical profiles of 1254 PCB measured in box core sediment samples collected off the JWPCP submarine outfalls, 1971. Station locations are shown in Figure 13.

February 1975. Corresponding decrease factors for total PCB in JWPCP effluent, and 1254 PCB in bottom sediments and Dover sole from the discharge monitoring zone (the closest comparison for which data are available), were 12.0, 1.6, and 1.4, respectively (Young et al., 1976f). These data suggest that coastal bottom sediments only slowly lose DDT and PCB compounds by which they have become contaminated. This conclusion is consistent with results of laboratory experiments described in detail in Appendix I.

These results further suggest that decreases in contamination levels of benthic organisms such as Dover sole follow decreases in sediment contamination levels rather than decreased inputs. On the order of 200 m tons of DDT residues still reside in the bottom sediments off Palos Verdes Peninsula, compared to the 1 m ton of DDT introduced there during 1975 by the JWPCP submarine outfalls. All other known inputs to the entire Bight total only about 2 m tons/yr. Thus, it appears that this sediment reservoir may now constitute the dominant source of DDT pollution to the ecosystem of the Bight.

The ecological importance of contaminating sediments with chlorinated hydrocarbons such as the DDT compounds is further highlighted by the following consideration. As discussed in Section V, the information available to us indicates that the predominant input of DDT residues to the CSDLAC sewer system from the Montrose Chemical Corp. pesticide plant decreased from approximately 300 kg/day to less than 0.3 kg/day between spring and fall of 1970. Nevertheless, the gradual flushing of contaminated sediments from the sewers to JWPCP caused this wastewater discharge five years later to remain the largest point source input of DDT residues to the Bight. In February 1975, levels of total DDT up to 110 ppm wet wt still were being found in Dover sole trawled from the contaminated ocean bottom sediments around the JWPCP outfalls. This value was more than 20 times the 5 ppm action guideline adopted by the U.S. Food and Drug Administration.

Representative contamination levels in bottom feeding fishes also have remained excessive over the study period. By grouping all our data for total DDT in muscle tissue of Dover sole trawled from the JWPCP monitoring zone in 1971-72 and 1974-75, we obtained median values of 9.0 and 12 ppm, respectively; for total PCB, the values were 1.9 and 1.3 ppm, respectively (McDermott and Heesen, 1975a). CSDLAC also found no significant decrease in the former parameter; the mean concentration for all available 1971-72 collections was 15.8 ppm, while mean concentrations measured in the fall 1974 and the spring 1975 CSDLAC collections were 13.8 ppm and 16.7 ppm, respectively. CSDLAC also found relatively small decreases in total DDT levels in muscle tissue of two other bottom feeding species (both popular sports fish) collected from the JWPCP monitoring zone. For the kelp bass (Paralabrax clathratus), no difference was obtained between the

fall 1971 and the spring 1975 means (6.4 ppm and 6.3 ppm, respectively). For the black perch (Embiotoca jacksoni), the mean value fell by a factor of 3.3, from 18.3 to 5.6 ppm, respectively (Douglas Hotchkiss, CSDLAC, personal communication). Over the same period, the "effective" total DDT input fell by a factor of 8.0 (Young et al., 1976f).

Water Column Contamination

The results of the studies described above illustrate the extent to which a point-source input of chlorinated hydrocarbon wastes may be distributed throughout a coastal marine ecosystem. They also illustrate the degree to which the benthic environment around such a source may become contaminated, the persistence of such contamination, and the influence sediment levels can have on corresponding levels of contamination in benthic organisms.

In light of the massive DDT contamination which has occurred around the JWPCP outfall system, and the significant PCB inputs which have occurred via this and the OCSD and Hyperion outfalls, we have developed an offshore biomonitoring system which can provide early warning of excessive water column contamination in such discharge zones.

The organism selected for this trial study was the intertidal mussel Mytilus californianus. Various species of this byssal mollusk have been successfully used in the past as indicators of coastal and island contamination by chlorinated hydrocarbons (de Lappe et al., 1972; Young and Heesen, 1974; McDermott et al., 1976), petroleum hydrocarbons (Clark and Finley, 1973; Disalvo et al., 1975), trace metals (Alexander and Young, 1976) and radionuclides (Young and Folsom, 1973). Mytilus is widely distributed in the temperate zone of the world ocean, large numbers can usually be collected at a variety of sites, and the sex can be identified easily. We have found that DDT and PCB residues are highly concentrated in the whole soft tissues of the bay species M. edulis in southern California. For example, levels of total DDT in surface seawater and intertidal mussels measured near the mouth of Los Angeles Harbor in 1974 were 10 parts per trillion (ng/l) and 1 part per million (mg/wet kg), respectively; PCB levels in these samples were lower by about a factor of ten. Thus, the organism appears to concentrate chlorinated hydrocarbons on the order of 100,000 times above seawater values (Young et al., 1976e).

In June, 1974, 1200 specimens of M. californianus, 4 to 6 cm in length, were collected from Point Sal, a relatively uncontaminated region approximately 250 km northwest of Los Angeles. They were transported alive to a special taut-line buoy system (Appendix I) that had been installed in 35 meters of water above contaminated sediments approximately 3 km northwest of the JWPCP submarine

outfalls. From this system, four nylon mesh bags, each containing about 60 mussels, were suspended at each of five depths below the surface: 0.5 m (surface), 4 m, 15 m, 25 m, 35 m (bottom). The bottom bags were hung within a metal mesh cage that rested directly on the sediments in the discharge field. At the time of the Point Sal collection, samples of 4 to 6 cm M. californianus also were obtained from the rocky intertidal zone at Royal Palm State Beach, located at the base of the JWPCP submarine outfalls. Fresh individuals from both collections were separated by sex, and six male and six female replicate composites of whole soft tissues from five mussels were analyzed.

Specimens were collected from each level of the buoy system every seven days for the first seven weeks; thereafter, they were collected every fourteen days. The whole soft tissues (excluding byssal threads) were excised from five males and five females from each level while the specimens were still fresh. The tissues were then drained, homogenized and ten composite samples, one male and one female composite from each level, were analyzed for DDT and PCB concentrations. To minimize the effect of varying water content, aliquots of the homogenates were dried overnight at 60°C to obtain individual dry to wet weight ratios (the average ratio calculated was 0.28 $\pm$ 0.02 at the 95 percent confidence level).

Mean concentrations of total DDT and total PCB, and their standard errors, in the male and female replicates from the outfall (Royal Palm) and control (Point Sal) regions are listed in Appendix I. These data show that, on the average, mussels living inshore of the buoy contained roughly 50 times as much total DDT and 16 times as much total PCB as did the Point Sal specimens (0.11 and 0.05 ppm dry wt , respectively) at the time of their transfer to the buoy northwest of the outfalls. Thus, exposure of the Point Sal mussels to chlorinated hydrocarbons was greatly increased upon their transfer to the discharge region.

At the time of their transfer, there was no significant difference, at the 95 percent confidence level, between the male and female levels of total DDT and total PCB. A paired t-test was utilized to determine if the rate of DDT and PCB uptake was sex dependant. Over time, no statistically significant differences for these chlorinated hydrocarbons were observed between the sexes from any of the five levels ($p > 0.10$). The means of the male and female values were calculated and the resulting uptake curves for total DDT and total PCB are illustrated in Figures 15 and 16, respectively.

These results show that during the summer of 1974, there was a direct relationship between uptake of DDT and PCB and proximity of the bioindicators to the contaminated bottom sediments and to the wastewater plume which at that time was largely trapped beneath the thermocline. Within a period of one week, the

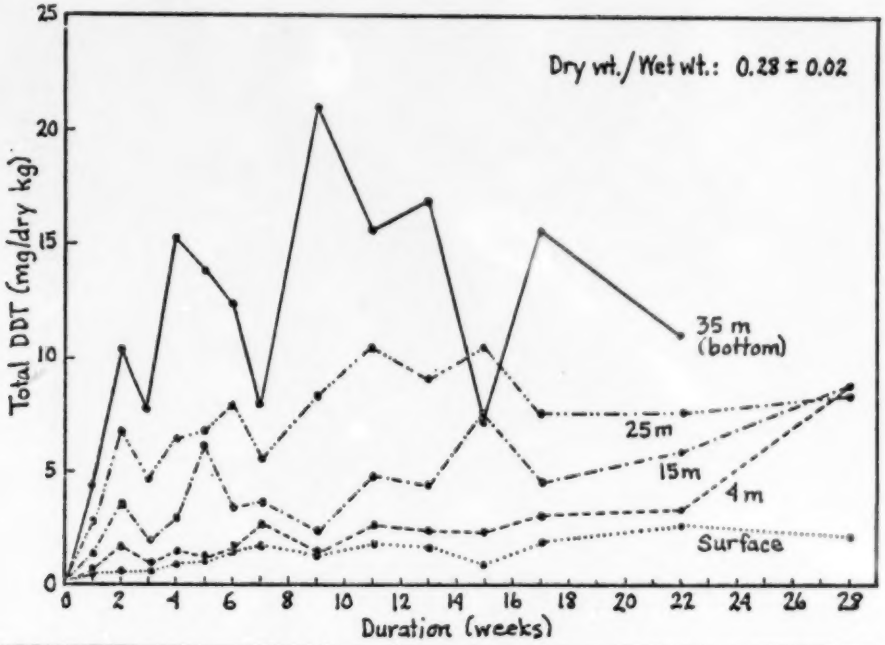

Figure 15. Uptake curves for total DDT in mussels translocated in June 1974 from Point Sal to the JWPCP outfall buoy system.

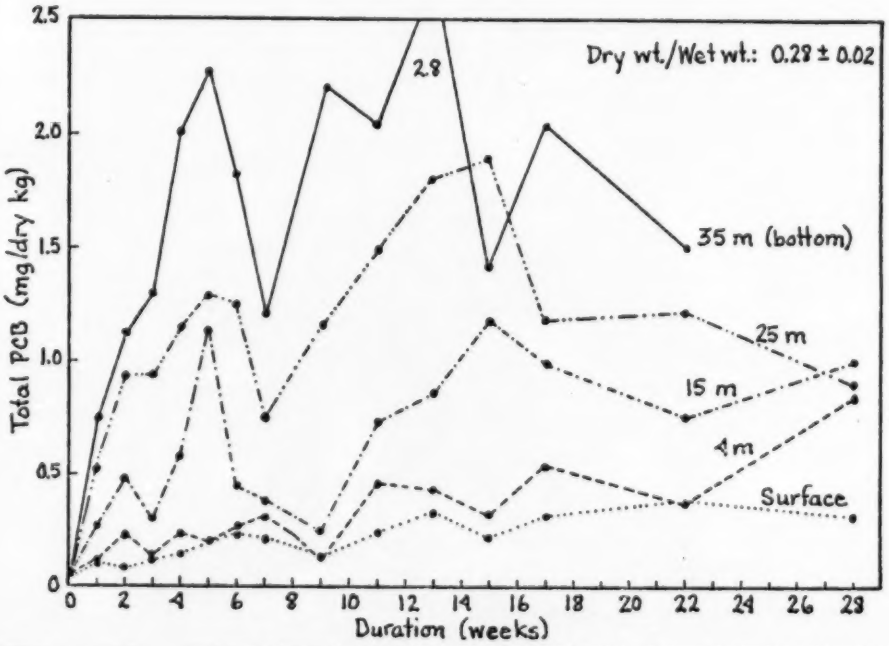

Figure 16. Uptake curves for total PCB in mussels translocated in June 1974 from Point Sal to the JWPCP outfall buoy system.

specimens from the bottom had increased their levels of DDT and PCB by factors of 43 and 18, respectively; those from the surface increased their levels by factors of 5 and 3, respectively. Throughout the uptake study, there were periods when the organisms appeared to rid themselves of a portion of their chlorinated hydrocarbon burden. Part of the variability observed, such as the dip in some of the curves at week seven, may be due to spawning; alternatively, the cause may have been movement of the wastewater plume away from the buoy system. Halfway through the twenty-eight week experiment, the bottom and surface specimens respectively had accumulated total DDT to levels approximately 200 and 20 times greater than those measured in the controls; corresponding contamination factors for total PCB were 60 and 6. At this point uptake in specimens from the two deepest levels (35 m and 25 m) ceased, and there was some indication of a subsequent decrease in their DDT and PCB concentrations. In contrast, values for the next two stations (15 m and 4 m), and to some extent for the surface station also, continued to increase. This is consistent with a weakening of the thermocline in the fall season and a corresponding increase in exposure of the upper specimens to the wastewater plume in the mixed layer of the discharge zone.

To further examine this effect, we repeated the experiment in the winter season, and expanded it to also include the discharge regions of the Hyperion 7-mile sludge outfall at the mouth of Santa Monica Submarine Canyon in Santa Monica Bay, and the OCSD 5-mile outfall off Newport Beach. Together these three municipal outfall systems account for approximately 85 percent of the municipal wastewater discharged to the Southern California Bight, and more than 90 percent of the 1975 input of chlorinated hydrocarbons measured in the major submarine discharges.

On January 14, 1976 several thousand small (4-6 cm) mussels were collected from the Point Sal control site and transferred to a buoy system located 2 km to the northwest of the OCSD outfall diffuser. Four culture bags, each containing 60 mussels, were hung at the following depths: 0.5, 15, 30, 45 and 60 meters. The bottom samples again were protected in a cage resting on the sediments. Efforts to similarly place mussels at two JWPCP buoys, respectively located 1-2 km to the southeast (30 m) and northwest (60 m) of the outfalls, failed when part of the latter system was discovered to be missing. Therefore, another mussel collection was conducted at Point Sal on January 28, 1976 during the next available low tide. The two JWPCP mussel buoys systems were activated at levels of 0.5, 10, 15, 20, and 30 m, and at 0.5, 15, 30, 40 and 60 m, respectively. Samples were subsequently collected at the lower four levels of the inshore buoy, but the outer buoy, which is highly traveled by trawlers, again was hit and the mussels lost. However, samples were successfully collected at 0.5, 15, 45, 75, and 90 m on the buoy system located within 1 km of the Hyperion 7-mile sludge discharge, which was also activated on January 28.

In addition, during January local mussels were collected at the nearest inshore station of the three buoy systems. Resultant concentrations in the Point Sal and local coastal mussel replicate composites are presented in Appendix I. During each buoy collection attempts were made to collect water samples at each depth for analysis of NH_4-N, and BT temperature profiles also were usually obtained to aid in evaluation of the extent of mussel exposure to the wastewater plumes.

The resulting uptake distributions in the Palos Verdes buoy mussels are illustrated in Figures 17 and 18; more detailed information is presented in Appendix I. These data indicate that halfway through the twelve-week experiment, an approximate steady state condition had been reached. The apparent equilibrium concentrations of total DDT and total PCB in the bottom specimens (approximately 7 and 1 ppm dry wt., respectively) were about half those estimated from the previous experiment. This is consistent with the fact that the first buoy system was located to the northwest ("downcurrent") of the JWPCP diffusers, in a more contaminated region than this buoy system which was situated southeast of the outfalls. Surface sediment total DDT concentrations measured at the buoy sites near the end of the two experiments were 10 and 3.5 ppm dry wt., respectively; corresponding values for total PCB were 0.64 and 0.25 ppm.

However, the most significant finding of this second (winter) experiment was that the steep vertical gradients in DDT and PCB uptake levels seen during the first (summer) experiment were greatly reduced. Whereas bottom specimen concentrations previously had exceeded those at the surface by a factor of 10, corresponding concentrations observed in these experiments at all four levels generally agreed within a factor of 2. Further, in contrast to the first experiment, relative concentrations were not strongly correlated with depth; the middle (15 m) specimens often contained concentrations equal to or exceeding those measured in the bottom (30 m) mussels. A similar result was observed in the uptake curves for total PCB off the OCSD outfall (Figure 19).

These results are consistent with the temperature and ammonium profiles which we measured off the three outfall sites during the winter uptake experiments. No significant thermocline developed which could have significantly capped the rising wastewater plumes, and the NH_4-N concentrations generally indicated good mixing throughout the water column.

Figure 20 illustrates the PCB results observed off the mouth of the 7-mile Hyperion sludge outfall. In this case, there was a much stronger correlation between concentration and depth. This would seem to be the result of the high solids content (approximately 7500 ppm) of the sludge (compared to the 100-300 ppm

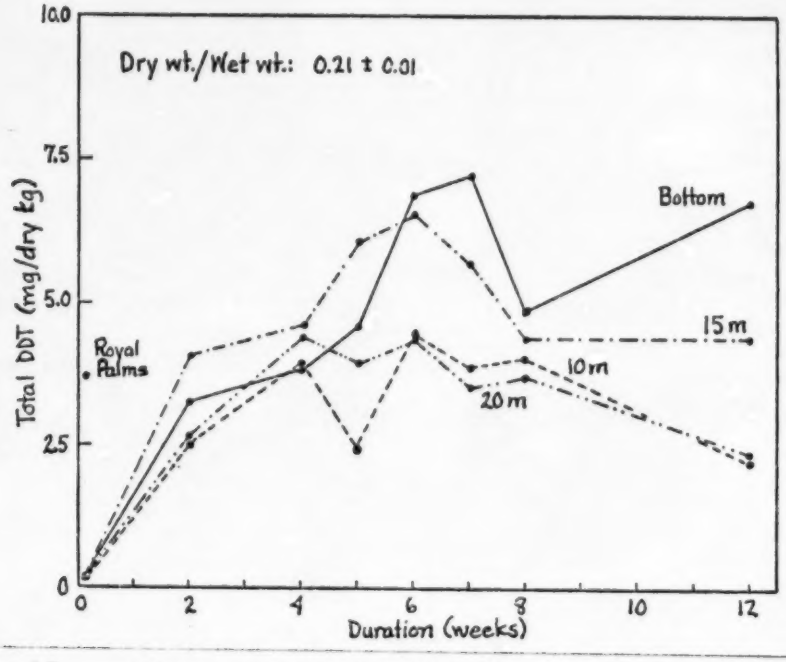

Figure 17. Uptake curves for total DDT in mussels translocated in January 1976 from Point Sal to the JWPCP outfall buoy system.

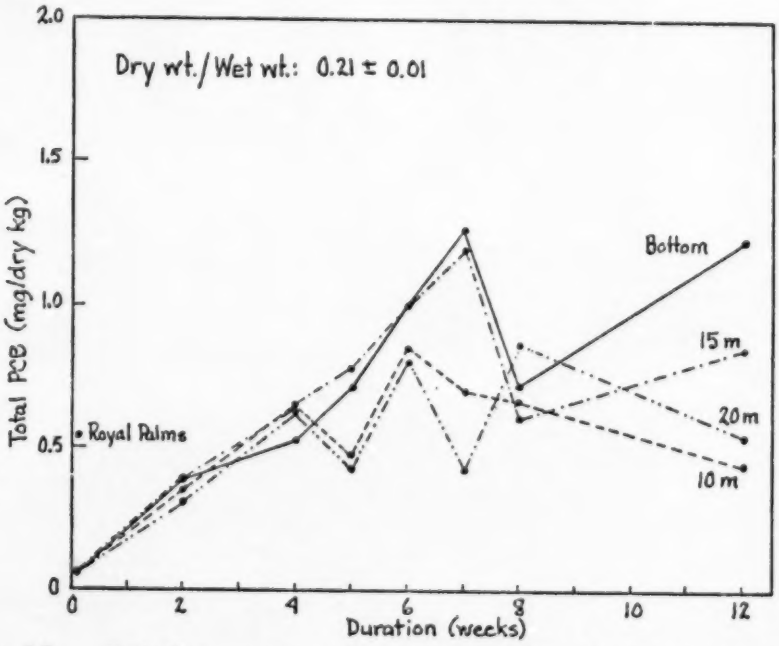

Figure 18. Uptake curves for total PCB in mussels translocated in January 1976 from Point Sal to the JWPCP outfall buoy system.

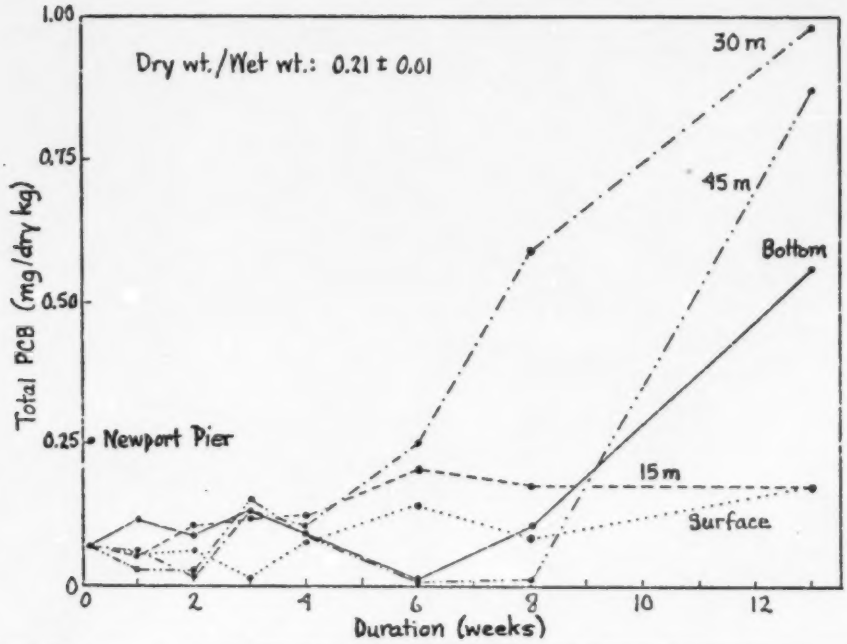

Figure 19. Uptake curves for total PCB in mussels translocated in January 1976 from Point Sal to the OCSD outfall buoy system.

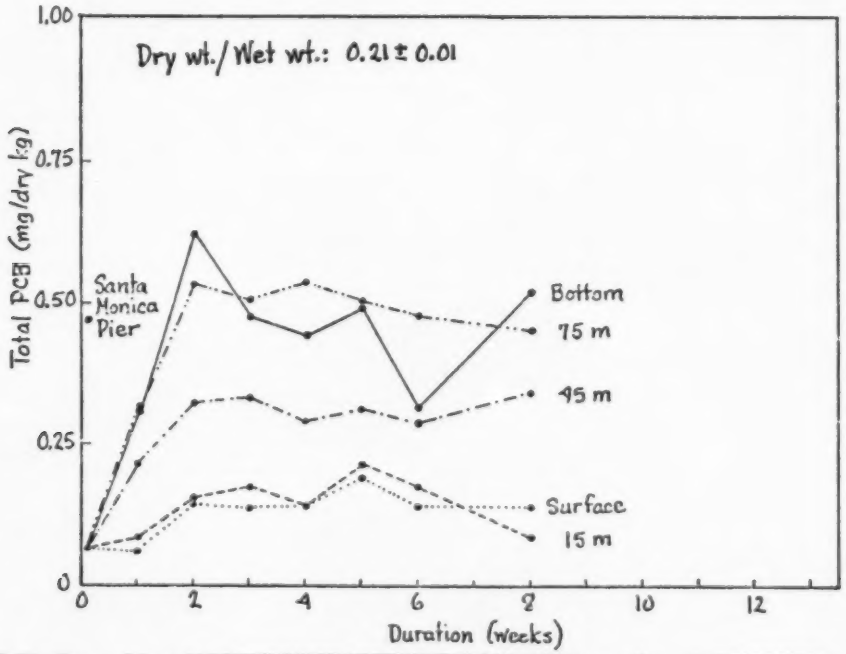

Figure 20. Uptake curves for total PCB in mussels translocated in January 1976 from Point Sal to the Hyperion sludge outfall buoy system.

concentrations of the other two effluents), which works against vertical mixing of the wastewater particulates carrying a large majority of the PCB contaminants.

Finally, the distributions of total DDT in the mussels suspended near both the OCSD and Hyperion outfalls showed no relation with depth, and, in contrast to the case for total PCB, final concentrations in the bottom level mussels were less than half those measured in the intertidal specimens collected at the base of the outfalls (Appendix I). This is consistent with the fact that these outfalls are not significant sources of DDT residues relative to the JWPCP outfalls situated approximately midway between them. (Total DDT concentrations in surface sediments at the OCSD and Hyperion buoy sites were 0.009 and 0.052 ppm, respectively; corresponding values for total PCB were 0.086 and 0.43 ppm).

Discussion

The results of the buoy experiments indicate that it is the wastewater plume rather than the contaminated bottom sediments which is the source of chlorinated hydrocarbon uptake seen in the filter-feeding mussels cultured throughout the water column. The highest total PCB level reached near any of the three major outfalls studied was about 0.5 ppm wet wt (2 ppm dry wt), an order-of-magnitude below the federal guideline for seafood. In comparison, concentrations of this contaminant in bottom-feeding crabs and flatfish collected from these discharge zones generally have not exceeded 2 ppm wet wt in recent years, and median concentrations of both total DDT and total PCB typically have been on the same order as those found in the bottom sediments (Young et al., 1975b; Young et al., 1976a).

Although the present submarine discharges are not causing DDT or PCB levels in seafood organisms to exceed the 5 ppm action guideline, recent findings suggest that this limit may be too high. Allen et al. (1976) have shown that dietary levels of 1248 PCB as low as 2.5 ppm inhibit reproduction in nonhuman primates, and we recently have demonstrated that muscle tissue concentrations of 2 ppm total PCB are significantly correlated with the occurance of fin erosion disease in Dover sole (McDermott-Ehrlich et al., 1976).

SECTION XIII

CHLORINATED BENZENES

During the course of our investigation into levels of chlorinated pesticides and PCB's in major municipal wastewaters of southern California, several other chlorinated compounds of potential concern were uncovered. The first was hexachlorobenzine (HCB), which was tentatively identified by project consultants R. Risebrough and B. de Lappe (Bodega Marine Laboratory) during the spring 1974 wastewater intercalibration. Subsequently, this signal was repeatedly observed in our semi-annual analyses of final effluent by electron capture gas chromatography (gc/ec). A summary of the tentative quantifications is presented in Appendix J. These results, obtained over a two-year period with four different columns in two different laboratories, were in sufficient agreement to indicate that HCB levels are one to two orders of magnitude below those measured for PCB in these wastewaters (Table 1). This is important in view of the growing concern about HCB in the environment (NAS, 1975).

However, we also have identified four other chlorinated benzenes which appear to have received much less attention in ocean pollution studies. These are para-dichlorobenzene (p-DCB), ortho-dichlorobenzene (o-DCB), 1,2,4-trichlorobenzene (1,2,4-TCB), and 1,3,5-trichlorobenzene (1,3,5-TCB); the results from our two 1975 seasonal surveys (Table 9) suggest that all except the last occur at concentrations which are at least an order-of-magnitude above those of HCB, comparable with observed PCB levels.

TABLE 9. ESTIMATED CHLOROBENZENE CONCENTRATIONS (µg/l) IN MAJOR MUNICIPAL WASTEWATERS, 1975

CB	JWPCP		Hyp-5 mi		Hyp-7 mi		OCSD		Pt. Loma		Oxnard	
	Sum.	Fall	Sum.	Fall	Sum.	Fall	Sum.	Fall	Sum.	Fall	Sum.	Fall
p-DCB	7.4	12	3.4	5.1	34	230	4.9	-	-	0.42	9.3	3.1
o-DCB	7.3	12	1.9	4.0	30	440	2.4	-	2.2	<0.01	4.7	2.3
1,2,4-TCB	6.0	1.8	5.7	3.1	275	130	0.3	-	0.23	<0.01	0.9	0.25
1,3,5-TCB	0.2	0.8	<0.01	<0.01	0.9	<0.2	0.02	-	0.02	<0.01	0.4	<0.01
HCB	0.4	0.2	0.07	0.01	1.9	6.8	0.04	-	0.01	0.01	0.4	0.04
Total CB	21	27	11	12	340	800	7.7	-	2.5	0.4	16	5.8
Total PCB	1.2	1.6	0.3	0.4	63	18	5.8	8.7	1.6	1.7	0.2	0.3

In view of the uncertainty in identifying compounds by gc/ec retention times alone, we sought confirmation of these chlorinated benzenes by mass spectrometry. During January 1976 relatively large grab samples of JWPCP, OCSD, and Hyperion 7-mile "sludge" effluent were collected, and several replicate sets (representing volumes of 10 *l*, 10 *l*, and 1 *l*, respectively) were extracted and processed as described in Appendix A. Parallel treatment of corresponding standards indicated only second-order losses during this procedure.

One set of these samples was analyzed by gc/ec at our laboratory, according to the same procedure used for the earlier analyses of chlorinated benzenes in wastewater. Two other sets were submitted to California Analytical Laboratories (CAL) in Sacramento, California, and the EPA Environmental Research Laboratory in Athens, Georgia. At CAL the samples were analyzed by mass fragmentography as described in Appendix A. Confirmation of all of the chlorobenzenes under consideration except 1,3,5-TCB was obtained on the joint basis of retention time and corresponding detection of the molecular ions of the compounds; it is unlikely that other compounds with the m/e ratios of the chlorinated benzenes of interest would elute at the same times as these compounds. The presence of DCB in all three samples and TCB in the Hyperion sludge sample was also confirmed by the Athens laboratory.

Table 10 presents a quantitative comparison of the independent analyses of these wastewater samples by gc/ec at SCCWRP and gc/ms at CAL. With the exception of the DCB levels in the Hyperion sludge sample, the agreement between the two sets of data is most satisfactory. Thus, it appears that our identification of chlorinated benzene contamination of southern California municipal wastewater in general has been confirmed, although further work is needed to establish typical levels in individual cases.

TABLE 10. MUNICIPAL WASTEWATER CHLOROBENZENE CONCENTRATIONS (µg/l) DETERMINED BY ELECTRON-CAPTURE GAS CHROMATOGRAPHY (gc/ec) AND MASS SPECTROMETRY (gc/ms)

	JWPCP		Hyp. 7-mi.		OCSD	
Chlor Benzene	gc/ec	gc/ms	gc/ec	gc/ms	gc/ec	gc/ms
p-DCB	7.6	7.4	90	7.8	2.8	-
o-DCB	5.1	3.3	183	14	1.3	-
1,2,4-TCB	0.58	0.54	86	34	0.08	-
1,3,5-TCB	<0.01	-	0.3	-	0.001	-
HCB	0.10	0.05	0.45	0.41	0.010	0.007
Total CB	13	11	360	56	4.2	-

To examine the importance of surface runoff as a source of chlorobenzenes to the coastal ecosystem, we re-sampled the Los Angeles River during a major storm in 1976. As discussed earlier in the report, this channel had been found to be the single most important route of chlorinated hydrocarbon input via runoff to the Bight. Eleven samples collected during the February 6-9 rainstorm were obtained with an all-metal depth-integrating sampler and analyzed.

The mean net concentrations obtained for total DDT, 1254 PCB, and 1242 PCB were 0.34, 0.49, and < 0.18 ppb, respectively; only secondary blank corrections were necessary. These results were consistent with those measured for earlier storm collections from this channel (Table 4). Much lower concentrations of the chlorobenzenes were measured in a composite of these storm runoff samples, as seen below.

Chlorinated Hydrocarbon	Est. Net Conc. (µg/l)	Blank (µg/l)
p-DCB	0.05	0.044
o-DCB	0.01	0.024
1,2,4-TCB	0.005	0.001
1,3,5-TCB	0.004	0.003
HCB	0.001*	-
	$\bar{x} \pm$ S.E.	$\bar{x} \pm$ S.E.
Total DDT	0.34 ± 0.06	<0.004
1254 PCB	0.49 ± 0.09	0.004 ± 0.001
1242 PCB	0.18	0.005 ± 0.001

Comparison of these results with those of Tables 1 and 9 indicates that, in contrast to the case for municipal wastewater, inclusion of the chlorinated benzenes (CB) would constitute only a second-order addition to our normal estimate of TICH (total identifiable chlorinated hydrocarbons), i.e. the sum of total DDT, Dieldrin and total PCB. This CB/TICH ratio for the Los Angeles River runoff composite is 0.09, while the corresponding ratios obtained from our 1975 data for JWPCP and OCSD final effluent are 6.5 and 1.0, respectively. In view of these results and the fact that we have found surface runoff to be only a secondary input of TICH relative to that from municipal wastewater, it appears that urban runoff probably makes an insignificant contribution of these chlorinated benzenes to the Bight relative to those from our submarine outfalls.

As discussed earlier in this report, we have found that dry aerial fallout is an important source of total DDT and 1254 PCB to the Bight. Recently we conducted a pilot study into the importance of chlorobenzene inputs via this route. Five stations (Santa Barbara, El Segundo, La Jolla, Catalina Island, San Clemente Island) were selected which formed two transects that were parallel and roughly perpendicular to the coast, and extended

*Gross value

over much of the area sampled so intensively in our previous fallout studies. Both the unoiled iced fallout sampler described in Section X and a high-volume air sampler (composed of a glass-fiber filter and five layers of polyurethane foam pads) were deployed together, generally over 48-hour intervals during spring 1976. (The sampling interval was 24-hours at El Segundo, a region of relatively high industralization on the coast of Santa Monica Bay). Appendix A further describes the procedures used.

The high-volume air sampling data shown in Table 11 for the El Segundo-Catalina Is.-San Clemente Is. transect indicate significant differences between the characteristics observed for total DDT-1254 PCB and for the chlorinated benzenes. Levels of the

TABLE 11. CHLORINATED HYDROCARBONS (ng) MEASURED IN HIGH-VOLUME AIR SAMPLES COLLECTED OFF LOS ANGELES BASIN, 1976+

El Segundo Feb. 26-27	Filter (net)	Foam Pads (net) 1st	3rd	5th	Process Blanks Filter	Foam
p-DCB	<62*	1,600*	200*	240*	145	2,090
o-DCB	<14*	500	<15	48	28	22
1,2,4-TCB	< 6*	37	51	30	< 6	30
1,3,5-TCB	< 3*	21	12	22	< 3	7
HCB	< 1*	225	248	68	< 1	< 0.2
Total DDT	610	2,630	< 8	<17	<13	<12
1254 PCB	390	4,220	73	6	<22	22
		Foam Pads (net)			Process Blanks	
Catalina Is. April 6-8	Filter (net)	Ave. 1st 2nd, 3rd	4th	5th	Filter	Foam
p-DCB	103	100*	150*	100*	428	660
o-DCB	-	56	68	30	945	5
1,2,4-TCB	< 2*	14	18	12	< 1.5	9
1,3,5-TCB	<3	44	6	< 0.3	11	<0.2
HCB	0.2*	35	27	22	0.2	0.8
Total DDT	4	260	10	18	4	8
1254 PCB	14	1,420	48	260	16	25
San Clemente Is. March 15-17						
p-DCB	38	250	850	70	80	350
o-DCB	< 2.6*	< 2	< 6	< 1	< 2.6	< 2.6
1,2,4-TCB	< 1.0	5	15	1	< 1.0	18
1,3,5-TCB	< 0.4	< 1	< 1	< 1	<0.4	1.3
HCB	< 0.2	55	60	54	<0.2	4.4
Total DDT	18	620	2	13	<1.8	7
1254 PCB	15*	1,560	13	120	28	24

+ Approximately 2000 cu m sampled per 24-hour day
* Gross value

former contaminants on both the filter and the foam pads usually were at least an order-of-magnitude above those of the CB's. (The major exception is p-DCB, whose values are often questionable owing to relatively high and variable blanks). Also, most of the total DDT and 1254 PCB sampled was found on the front layers of the foam pad packet, indicating good sampling efficiency. In contrast, the quantities of a particular CB captured by the successive layers of foam were often much more uniform, suggesting either that significant percentages of the individual chlorobenzenes present were carried on through the sampler (eg., HCB), or that the interpretation is uncertain owing to similarities between the very low (nanograde) levels measured and corresponding blanks (eg., 1,2,4-TCB). These differences are consistent with the dry fallout data for the five sampling sites, summarized in Table 12. The rates measured for total DDT and 1254 PCB values exceeded those for the CB's by one-to-three orders of magnitude. The typical fallout rate for HCB (1 ng/m^2-day) was less than 1 percent of the median value measured for total DDT or 1254 PCB. In contrast, the estimated total quantity of HCB collected from the air samples by the foam pads was approximately 10-25 percent of the total DDT collected. Thus, it appears that the higher volatility of the chlorinated benzenes compared to the DDT and PCB compounds makes it much less likely that the CB's will be carried from the atmosphere to the coastal plain or waters of the Bight via dry particulate fallout.

TABLE 12. AERIAL FALLOUT OF CHLORINATED HYDROCARBONS OFF SOUTHERN CALIFORNIA - SPRING 1976 (ng/m^2-DAY)

	El Segundo *	Catalina Island	San Clemente Island	La Jolla	Santa Barbara	Median
p-DCB	-	-	-	-	-	-
o-DCB	-	<8	27	-	<53	<27
1,2,4-TCB	<20	-	<3	<2	<19	<11
1,3,5-TCB	-	<1	<3	<10	<8	<6
HCB	0.9	1.7	0.1	3.4	0.9	1
Total DDT	640 **	73	280	30	820	280
1254 PCB	860	230	98	78	170	170
1242 PCB	<260	<70	<150	<180	<250	<180

* Medians of six collections made during fall 1975
** The median value measured for Dieldrin was 10 ng/m^2-day

The chlorinated benzenes are an industrially important class of compounds. In the period 1955-61, approximately 13 percent of the benzene consumption in the U.S. was for production of chlorobenzenes (Hardie, 1964). Both p-DCB and o-DCB are manufactured in very large quantities; 1972 production figures in this country were 35 million kg and 28 million kg, respectively (IARC, 1974b). These exceed the 1971 value of 20 million kg for DDT (IARC, 1974a). In comparison, 1972 combined DCB production in Western Europe and Japan was 30 million kg and 27 million kg, respectively. Over 90 percent of the p-DCB consumed in the U.S. is in products in which use is made of the vapor produced by sublimation, such as moth repellant, mildew retardent, and space deodorizer (IARC, 1974b). It's common application as deodorant cakes in public urinals may well account for the relatively large concentrations which we have measured in municipal wastewaters. Results of a recent study on para-dichlorobenzene in fat fissue of Toyko residents are consistent with our observations that p-DCB is a widespread and relatively-important urban contaminant; the average concentration found in 34 samples was 2.3 ppm, compared to a value of 2.1 ppm for PCB, and levels measured in the blood were about three times the corresponding PCB concentrations (Morita and Ohi, 1975).

Uses of o-DCB have included cleaning solvents for engine parts, heat transfer media, rust proofing and degreasing agents, solvents for lacquers and resins, dye intermediates, and insectisides (Hardie, 1964). The trichlorobenzenes have been used for solvents of oil-soluble dyes and grease, dielectric fluds, lubricative oil additives, and termite extermination. A liquid mixture sold in the United Kingdom contained approximately 85 percent 1,2,4-TCB, 7 percent 1,2,3-TCB, and small amounts of 1,3,5-TCB, dichloro-, and tetrachlorobenzines (Hardie, 1964). This high ratio of 1,2,4- to 1,3,5-TCB is consistent with that observed in our southern California municipal wastewaters. The tetrachlorobenzenes are reported to have few industrial applications (Hardie, 1964).

In past years hexachlorobenzene has received considerable attention as an environmental contaminant; a recent report from the National Academy of Sciences concludes that this synthetic organic is a pollutant of special concern (NAS, 1975). It's use as a fungicide in seed treatment resulted in wildlife losses in the Netherlands, and accidental consumption of HCB-treated wheat in Turkey caused 3000-5000 cases of porphria, a disturbance of the metabolic pathway of heme synthesis. Approximately 7 thousand kg were used as a grain fungicide in 1971, principally in the western U.S.; apparently this is the only production data available. However, HCB has been detected in poultry and meat from twenty states, and 20,000 cattle were quarantined in Louisianna in 1972 when the 0.3 ppm action guideline for meat was exceeded. Concentrations of 1 ppm and 6 ppm have been measured in human fat tissue samples from Australia and Germany; respectively (NAS, 1975).

It is reported that HCB is also produced as a by-product in the manufacture of many chlorinated hydrocarbons, such as perchloroethylene and carbon-tetrachloride. If the amount of HCB produced by this process were equivalent to 0.1 percent of the total production of the low molecular weight hydrocarbons, yearly production would exceed 1 million kg. Thus, industrial wastes may be the major source of HCB to the environment (NAS, 1975).

In view of the emphasis which the National Academy of Sciences report has placed on HCB as a potential pollutant, and the relatively low HCB concentrations which we have measured compared to some of the other chlorinated benzenes, it seems useful to further compare these compounds. The 1974 Toxic Substances List (HEW, 1974) reports the following values (mg/kg body wt.) for median lethal oral dose to rats: Benzene, 3400; chlorobenzene, 2910; p-dichlorobenzene, 500; 1,2,4-trichlorobenzene, 756; 1,2,4,5-tetrachlorobenzene, 1500; hexachlorobenzene, 3500. Corresponding values for DDT residues and the PCB;s are: p,p'-DDT, 113; p,p'-DDE, 880; p,p'-DDD, 400; Arochlor 1232, 4470; Arochlor 1254, 500. In addition, Reid et al. (1973) found that, with rats under chronic exposure, o-DCB was considerably more toxic than p-DCB to the liver, one of the organ systems most affected by animal exposure to chlorobenzenes. These data suggest that p-DCB, o-DCB, and 1,2,4-TCB, three of the most abundant chlorinated hydrocarbons found in the southern California municipal wastewaters investigated may be as important as other hydrocarbons of present concern.

Although acute toxicity data for rodents are useful for such comparisons, we need information about long-term effects from low level exposure of these toxicants to marine organisms. Compounds such as p-DCB have been known for many years to be mitostatic poisons, causing disorders of cell division leading to inhibition of cell wall formation and consequently binucleate or multinucleate cells (Biesele, 1958). Unfortunately, very little research has been conducted on reproductive inhibition of marine organisms by chronic exposure to such compounds. One study reported by Grosch (1973) involved the effect of a 24-hour acute exposure of adult brine shrimp (Artiemia salina) to 10 ppm 1,3,5-TCB. Although the survival of the adults exposed to TCB was greater than that obtained with the other organic toxicants, the overall reproductive performance of these adults, which was reduced by about a factor of 10, was the worst observed for the six compounds tested.

Thus, it appears that concern regarding chlorinated hydrocarbons in municipal and other wastewaters, which to date has dealt mainly with the chlorinated pesticides such as DDT and Dieldrin and with the PCB's, should be expanded to cover the chlorobenzenes as well. Attention recently has been brought to HCB in the environment, but the data discussed above indicate that other chlorinated benzenes of possible greater importance also are being discharged to our coastal marine waters.

SECTION XIV

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SECTION XV

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